PB80-167265

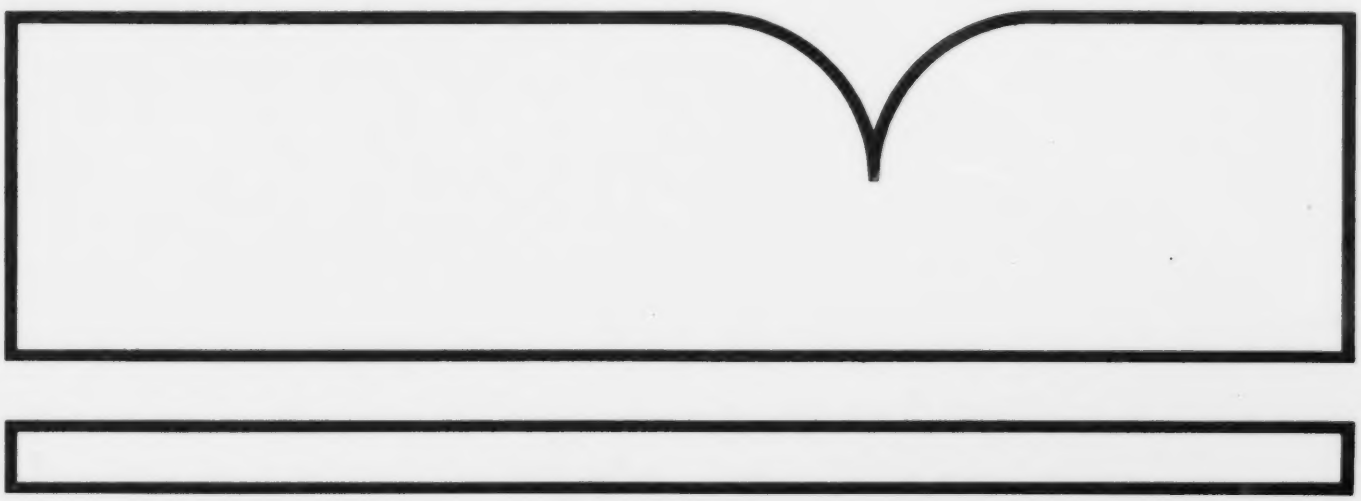
Materials Balance for 2,4-Diaminotoluene
Level I - Preliminary

JRB Associates, Inc.
McLean, VA

Prepared for

Environmental Protection Agency
Washington, DC Office of Toxic Substances

22 Feb 80



U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of
Toxic Substances
Washington, DC 20460

January 1980
EPA-560/13-79-016

Toxic Substances

PB80-167265

EPA

Materials Balance for 2,4 - Diaminotoluene

Review Copy

Level I - Preliminary

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA *Please read Instructions on the reverse before completing*		
1. REPORT NO. EPA 560/13-79-016	2.	3. RECIPIENT'S ACCESSION NO. PB 80 167265
4. TITLE AND SUBTITLE Materials Balance for 2,4-Diaminotoluene		5. REPORT DATE February 22, 1980 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Pauline Johnston, Ron Burger, Virginia Hodge, Karen Walker, Karen Slimak		8. PERFORMING ORGANIZATION REPORT NO. 2-800-03-379-24
9. PERFORMING ORGANIZATION NAME AND ADDRESS Survey and Analysis Division Office of Pesticides and Toxic Substances U.S. Environmental Protection Agency Washington, D. C. 20460		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-01-5793, Task #6
12. SPONSORING AGENCY NAME AND ADDRESS Office of Pesticides and Toxic Substances U.S. Environmental Protection Agency Washington, D. C. 20460		13. TYPE OF REPORT AND PERIOD COVERED Revised Final Report 14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES Michael Callahan, Project Officer		

16. ABSTRACT

The purpose of the Level I materials balance for 2,4-Diaminotoluene is to evaluate the sources of release of 2,4-DAT to the environment. 2,4-Diaminotoluene is produced commerically for use in the manufacture of 2,4-toluene diisocyanate and dyes. 2,4-Toluene diisocyanate (2,4-TDI) production is estimated to account for 99% of 2,4-DAT use. 2,4-Toluene diisocyanate is commercially manufactured for use in the production of urethane products, mainly polyurethane foams. 2,4-Diaminotoluene is produced directly through its manufacture and indirectly through the hydrolysis of 2,4-TDI and polyurethane foams, the metabolism of 2,4-dinitrotoluene, and the degradation of dyes. Small quantities of 2,4-DAT are imported into the U.S. directly and as a contaminant in 2,4-DAT-containing dyes. The major sources of release of 2,4-DAT to the environment are 2,4-DAT manufacture and 2,4-TDI hydrolysis. Minor sources of release are TDI production, the use of polyurethane foams, dye production and use, the import of 2,4-DAT and the export of TDI. Releases of 2,4-DAT appear to be greatest in areas of West Virginia and Louisiana. Of the 196,000 kkg of 2,4-DAT estimated to have been produced in 1977, greater than 10,600 kkg (5.4%) is estimated to have been released to the environment during that year.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS (*This Report*) Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS (*This page*) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

REVISED FINAL REPORT

LEVEL I MATERIALS BALANCE

2,4-DIAMINOTOLUENE

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICES OF PESTICIDES AND TOXIC SUBSTANCES
SURVEY AND ANALYSIS DIVISION
Task No. 6
Contract No. 68-01-5793
Michael Callahan - Project Officer
C. Richard Cothern - Task Manager

Prepared by:

JRB ASSOCIATES, INC.
8400 Westpark Drive
McLean, Virginia 22102

Project Manager: Karen Slimak

Task Leader: Pauline Johnston

Contributing Writers: Ron Burger
Virginia Hodge
Karen Walker

Submitted: February 22, 1980

1a

THE FINAL REPORT PRESENTED HEREIN RESULTED FROM A LEVEL I MATERIALS BALANCE STUDY ON 2,4-DIAMINOTOLUENE. THE RESULTS WERE BASED ON AN ANALYSIS OF LITERATURE SUPPLIED BY EPA. ALTHOUGH SUPPLEMENTARY INFORMATION UNDOUBTEDLY EXISTS, OBTAINING IT WAS OUTSIDE THE SCOPE OF THIS TASK. THE LEVEL I REPORT IS INTENDED TO SERVE AS A FOCUS OF DISCUSSION AND AS A BASIS FOR FUTURE MATERIALS BALANCE STUDIES; IT IS NOT MEANT TO BE A DEFINITIVE STUDY.

MATERIALS BALANCE LEVELS

Materials balance studies are performed at three levels or depths of study and effort. In general the study of a chemical proceeds sequentially through these three levels. Particular chemicals are assigned to be studied at one of the levels on the basis of availability of information. The three levels are described below.

Level I:

A LEVEL I MATERIALS BALANCE requires the lowest level of effort and involves a survey of readily available information for constructing the materials balance. Ordinarily, many assumptions must be made in accounting for gaps in information; however, all are substantiated to the greatest degree possible. Where possible the uncertainties in numerical values are given, otherwise they are estimated. Data gaps are identified and recommendations are made for filling them. A Level I materials balance relies heavily on the EPA's Chemical Information Division as a source of data and references involving readily available information. Most Level I MB's are completed within a 3-6 week period; CID literature searches generally require a 2 week period to complete. Thus the total time required for completion of a Level I materials balance ranges from 5-7 weeks.

Level II:

A Level II MATERIALS BALANCE involves a greater level of effort, including an in-depth search for all information relevant to the materials balance. The search includes all literature, (concentrating on primary references), contacts with trade associations, other agencies, and industry to try to uncover unpublished information, and possibly site investigations. Uncertainties and further data needs are identified in the Level II report. Recommendations for site sampling needs for Level III are also identified.

Level III:

A Level III study requires generation of new data through monitoring and other means. It builds on the Level II literature searches and reviews of industrial production data by filling in data gaps through site visits and necessary monitoring. The data generated in this type of study are intended to be statistically valid and have known confidence values. The goal is a study upon which regulations or legal proceedings may be based.

TABLE OF CONTENTS

		Page
	TABLE OF FIGURES	vi
	TABLE OF TABLES	vii
	EXECUTIVE SUMMARY	viii
1.0	INTRODUCTION	1-1
2.0	RELEASES FROM MANUFACTURING AND IMPORTS	2-1
	2.1 MANUFACTURE OF 2,4-DIAMINOTOLUENE	2-1
	2.1.1 Processes	2-1
	2.1.2 Releases to the Environment During 2,4-Diaminotoluene Production	2-2
	2.1.3 Producers	2-11
	2.2 RELEASES FROM IMPORTS OF 2,4-DIAMINOTOLUENE	2-11
	2.3 RELEASES FROM AMINE RECOVERY FROM POLYURETHANE FOAMS	2-13
	2.4 RELEASES FROM IMPORTS OF 2,4-TOLUENE DIISOCYANATE	2-13
	2.5 RELEASES FROM IMPORTS OF DYES	2-13
3.0	RELEASES FROM USES OF 2,4-DIAMINOTOLUENE	3-1
	3.1 RELEASES FROM PRODUCTION OF 2,4-TOLUENE DIISOCYANATE	3-1
	3.2 RELEASES FROM USES OF TOLUENE DIISOCYANATE	3-12
	3.2.1 Releases from Production of Polyurethane Foam Products	3-14
	3.2.2 Releases from Production of Other Polyurethane Products	3-15
	3.2.3 Releases from Export of Toluene Diisocyanate	3-16
	3.3 RELEASES FROM USE OF POLYURETHANE PRODUCTS	3-16
	3.3.1 Releases from Use of Polyurethane Foam	3-16
	3.3.2 Releases from Use of Other Polyurethane Products	3-16
	3.4 RELEASES FROM DYE PRODUCTION	3-16
	3.5 RELEASES FROM DYE PROCESSES	3-21
	3.6 RELEASES DURING EXPORT OF 2,4-DIAMINOTOLUENE	3-23
4.0	RELEASES FROM INDIRECT SOURCES OF DIAMINOTOLUENE	4-1
	4.1 HYDROLYSIS OF TOLUENE DIISOCYANATE	4-1
	4.2 HYDROLYSIS OF POLYURETHANE FOAMS	4-1
	4.3 METABOLISM OF 2,4-DINITROTOLUENE	4-4
	4.4 DEGRADATION OF DYES	4-5

TABLE OF CONTENTS (continued)

		Page
5.0	RELEASE SOURCE EVALUATION	5-1
6.0	DATA GAPS AND RECOMMENDATIONS	6-1
	6.1 MANUFACTURE OF 2,4-DIAMINOTOLUENE	6-1
	6.2 IMPORTS OF 2,4-DIAMINOTOLUENE	6-2
	6.3 EXPORTS OF 2,4-DIAMINOTOLUENE	6-2
	6.4 2,4-TOLUENE DIISOCYANATE PRODUCTION	6-2
	6.5 IMPORTS OF 2,4-TOLUENE DIISOCYANATE	6-3
	6.6 EXPORTS OF 2,4-TOLUENE DIISOCYANATE	6-3
	6.7 MANUFACTURE OF PRODUCTS FROM 2,4-TOLUENE DIISOCYANATE	6-3
	6.8 USES OF POLYURETHANE PRODUCTS	6-4
	6.9 DYE PRODUCTION	6-4
	6.10 IMPORTS OF DYES	6-4
	6.11 EXPORTS OF DYES	6-5
	6.12 DYE USAGE	6-5
	6.13 INDIRECT SOURCES OF 2,4-DIAMINOTOLUENE	6-6

TABLE OF FIGURES

Figure		Page
1	Flow Diagram for 2,4-Diaminotoluene	vi
2.1	Production of 2,4-Diaminotoluene	2-3
2.2	Producers of 2,4-Diaminotoluene	2-12
3.1	Producers of Toluene Diisocyanate	3-10
3.2	Toluene Diisocyanate Manufacture	3-11
3.3	Producers of 2,4-Diaminotoluene Dyes	3-22

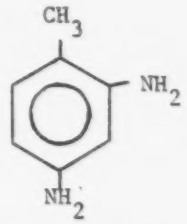
TABLE OF TABLES

Table		Page
1	Summary of Materials Balance for 2,4-Diaminotoluene	vii
2.1	Releases from Manufacture and Imports	2-4
3.1	Releases During Uses of 2,4-Diaminotoluene	3-2
3.2	Alternate Uses of Toluene Diisocyanate in 1976 and 1977, in Percent and kkg	3-13
3.3	1975 U.S. Rigid Urethane Foam Market in Percent and kkg Foam	3-13
3.4	2,4-Diaminotoluene Content of Flexible Polyurethane Foams	3-17
3.5	Dyes Produced from 2,4-Diaminotoluene	3-18
3.6	Estimate of the Maximum Amount of 2,4-Diaminotoluene Dyes Produced	3-20
4.1	Release from Indirect Sources	4-2
5.1	Breakdown of Release Sources	5-2

EXECUTIVE SUMMARY

GENERAL DESCRIPTION OF 2,4-DIAMINOTOLUENE

2,4-Diaminotoluene (2,4-DAT) is a synthetic organic chemical with the following structure:



The physical properties of this compound are shown in Appendix A. Two of its properties warrant some discussion. Since the vapor pressure of 2,4-DAT is low, there is a minimal risk of contaminating the environment through evaporation. However, since the chemical is very soluble in water, the potential for exposure through waste streams and other water ways is great.

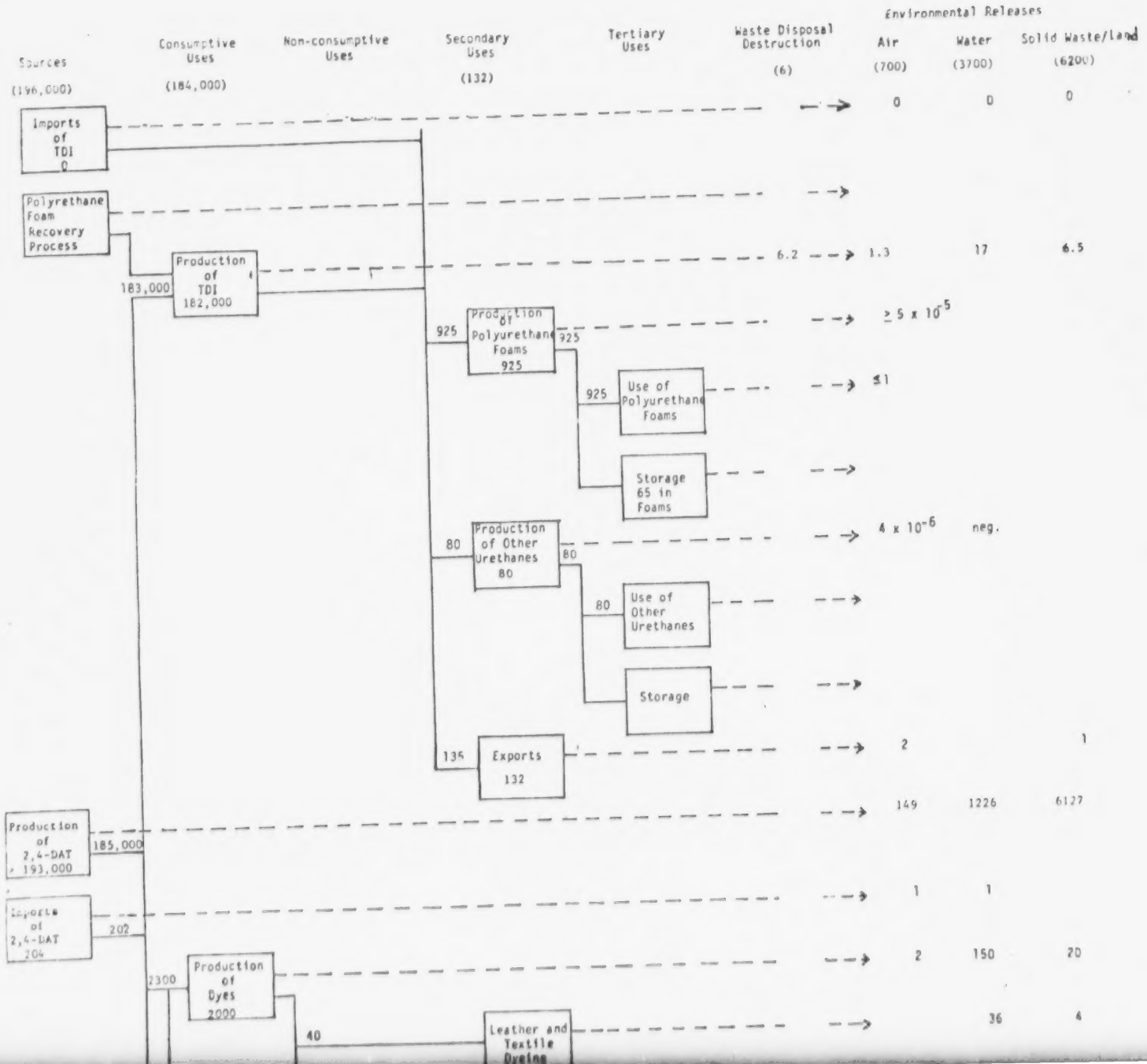
PRODUCTION AND PRIMARY USES

A minimum production figure for 2,4-DAT in 1977 was estimated using the amounts of 2,4-DAT consumed in the production of toluene diisocyanate (TDI) and dyes. This figure was 185,000 kkg. Small amounts of 2,4-DAT enter the country directly by import (204 kkg) or indirectly as a contaminant in imported dyes (0.3 kkg) (Figure 1).

Tne major use of 2,4-DAT (183,000 kkg) is in the production of TDI. Of the 229,000 kkg of TDI produced, approximately 81% was used in production of polyurethane foams, 7% was used in the production of other urethanes, and 12% was exported from the country.

A more minor use of 2,4-DAT is in the production of dyes. A maximum figure of 2,100 kkg of 2,4-DAT was estimated for use in production of dyes in 1977. In addition, some amount of 2,4-DAT is used directly in the dyeing process as a developer. This amount is unknown.

FIGURE 1 FLOW DIAGRAM FOR 2,4-DIAMINOTOLUENE



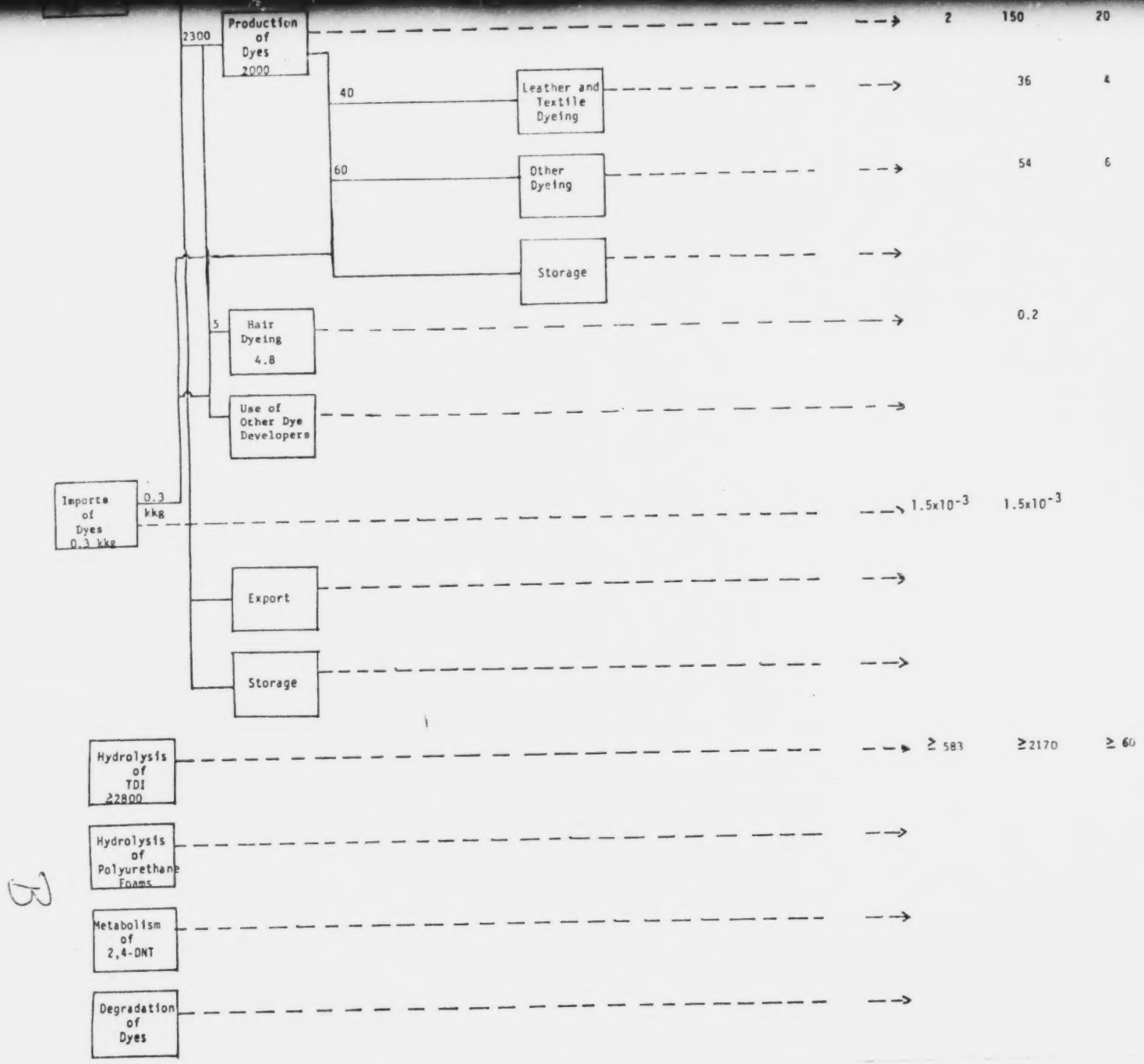

2300
Production of Dyes 2000
40
Leather and Textile Dyeing
60
Other Dyeing
Storage
5
Hair Dyeing 4.8
Use of Other Dye Developers
Imports of Dyes 0.3 kkg
0.3 kkg
Export
Storage
Hydrolysis of TDI 22800
Hydrolysis of Polyurethane Foams
Metabolism of 2,4-DNT
Degradation of Dyes
2
150
20
36
4
54
6
0.2
1.5x10-3
1.5x10-3
≥ 583
≥2170
≥ 60

TABLE 1 SUMMARY OF MATERIALS BALANCE FOR 2,4-DIAMINOTOLUENE

AMOUNTS PRODUCED = AMOUNTS CONSUMED OR DESTROYED + AMOUNTS STORED + AMOUNTS RELEASED

Amount Produced			
Direct Production	=	193,000	
Indirect Production	=	3,000	
			196,000
Amount Consumed or Destroyed			
Consumptive Uses	=	184,000	
Export	=	100	
Destruction	=	6	
			184,000
Amount Stored			
Storage	=	70	
Amount Released			
To Air	=	700	
To Land/Solid Waste	=	3,700	
To Water	=	6,200	
			11,000
AMOUNTS PRODUCED	=	196,000	
AMOUNTS CONSUMED OR DESTROYED; STORED; RELEASED	=	- 195,000	
NET		+ 1,000	

Information on quantities of 2,4-DAT which are stored or exported could not be obtained.

SUMMARY OF THE MATERIALS BALANCE FOR 2,4-DIAMINOTOLUENE

Of the 196,000 kkg of 2,4-DAT estimated to have been produced in 1977, a total of 10,600 kkg (or 5.4%) is estimated to have been released to the environment. The remaining 185,400 kkg are either exported, destroyed by combustion processes, or converted to other chemicals. Figure 1 provides a summary of the materials balance for 2,4-diaminotoluene. The flow of 2,4-DAT through the environment and the sources of releases are shown. The materials balance was based on 1977 data since production figures were not available for 1978.

The major source of release of 2,4-DAT occurs during DAT production (7,500 kkg). It is estimated that the majority of the 2,4-DAT released would be landfilled as solid waste with smaller amounts being released to water and air. A secondary major source of release is the hydrolysis of TDI. It is estimated that approximately 95% of TDI emitted during TDI production and use may be converted to DAT once it enters the environment. This would amount to greater than 2,800 kkg of 2,4-DAT being released due to TDI hydrolysis.

Other sources of release of DAT to the environment appear to be relatively minor. These sources include the production of TDI, polyurethanes, and dyes; the export of TDI out of the country; the imports of dyes and DAT into the country; and the use of polyurethanes and dyes.

Finally, the releases of 2,4-DAT to the environment from some processes is unknown. These processes include the use of 2,4-DAT as a dye developer, the hydrolysis of polyurethane foams, the metabolism of 2,4-dinitrotoluene, and the degradation of dyes. Of these sources of release of DAT to the environment, the degradation of dyes is considered to be the least significant.

It should be noted that the materials balance for 2,4-DAT does not balance (Table 1). For example, we estimate that as much as 925 kkg of 2,4-DAT may be present as an impurity in TDI and polyurethane foams. However, our present knowledge of the processes of foam production and use allow us to

account for only 66 kkg of this amount. These discrepancies may be resolved by further study and it is recommended that a Level II or III study be performed to more adequately assess the data.

1.0 INTRODUCTION

This report presents the results of a Level I Environmental Materials Balance for 2,4-diaminotoluene (2,4-DAT). This study was conducted for the Survey and Analysis Division of the U.S. EPA Office of Pesticides and Toxic Substances (OPTS). The primary objective of the study was to determine, within the constraints of time and information availability, the quantity of 2,4-diaminotoluene released to the environment annually, the sources of these releases, and the form in which 2,4-DAT is released.

By definition, a Level I materials balance involves a survey of readily available information supplied mostly by the Chemical Information Division of OPTS. It is expected in a Level I study that many assumptions and estimations must be made in accounting for all releases of the chemical to the environment. Therefore, the accuracy of the results is questionable, while at the same time being the best currently available.

The following procedure was used in conducting the environmental materials balance for 2,4-diaminotoluene:

1. Collect all readily available information provided by EPA on 2,4-DAT production processes, end-products, uses, disposal methods, handling procedures, environmental characteristics, etc.
2. Conduct initial examination of information.
3. Construct flow diagram of substance with emphasis on all points of release to the environment.
4. Extract quantitative data from literature. Recalculate and/or verify validity of data.
5. Identify data gaps.
6. Conduct follow-up data collection.
7. Complete materials balance making sound assumptions and engineering estimates.
8. Prepare written report.

The following pages represent the findings of this study. Section 2.0 explains the manufacture and imports of 2,4-DAT and examines all releases of 2,4-DAT to the environment during these processes. Section 3.0 describes the emissions related to all end-products and uses of 2,4-DAT following its production. Section 4.0 details the releases occuring during indirect production

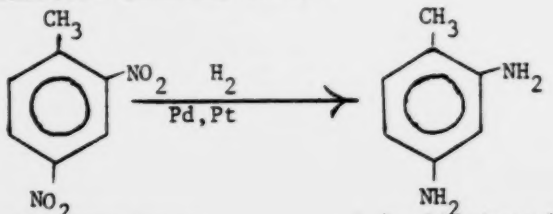
of 2,4-DAT. A summary of the releases of 2,4-DAT to the environment appears in Section 5.0. Finally, data gaps and recommendations for obtaining missing data appear in Section 6.0.

2.0 RELEASES FROM MANUFACTURE AND IMPORTS

2.1 MANUFACTURE OF 2,4-DIAMINOTOLUENE

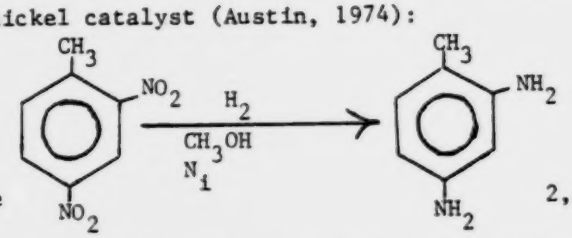
2.1.1 Processes

There are essentially two commercial methods for the production of 2,4-DAT. The first general method of 2,4-DAT production is the catalytic hydrogenation of dinitrotoluene. Two commercial processes exist. In the first operation, dinitrotoluene is reduced by liquid hydrogen in a reactor utilizing a platinum or palladium catalyst on charcoal (Austin, 1974):



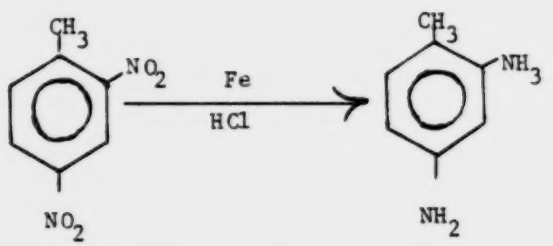
2,4-dinitrotoluene 2,4- diaminotoluene

In the second process, dinitrotoluene is dissolved in a methanol solution in the presence of a Raney nickel catalyst (Austin, 1974):



2,4- dinitrotoluene 2,4-diaminotoluene

The second method of 2,4-DAT production is by the reaction of hydrochloric acid with 2,4-dinitrotoluene in the presence of an iron catalyst (Austin, 1974). This reaction is illustrated as follows:



2,4-dinitrotoluene 2,4-diaminotoluene

Since it requires only simple equipment, this process is generally used by dye plants (Austin, 1974).

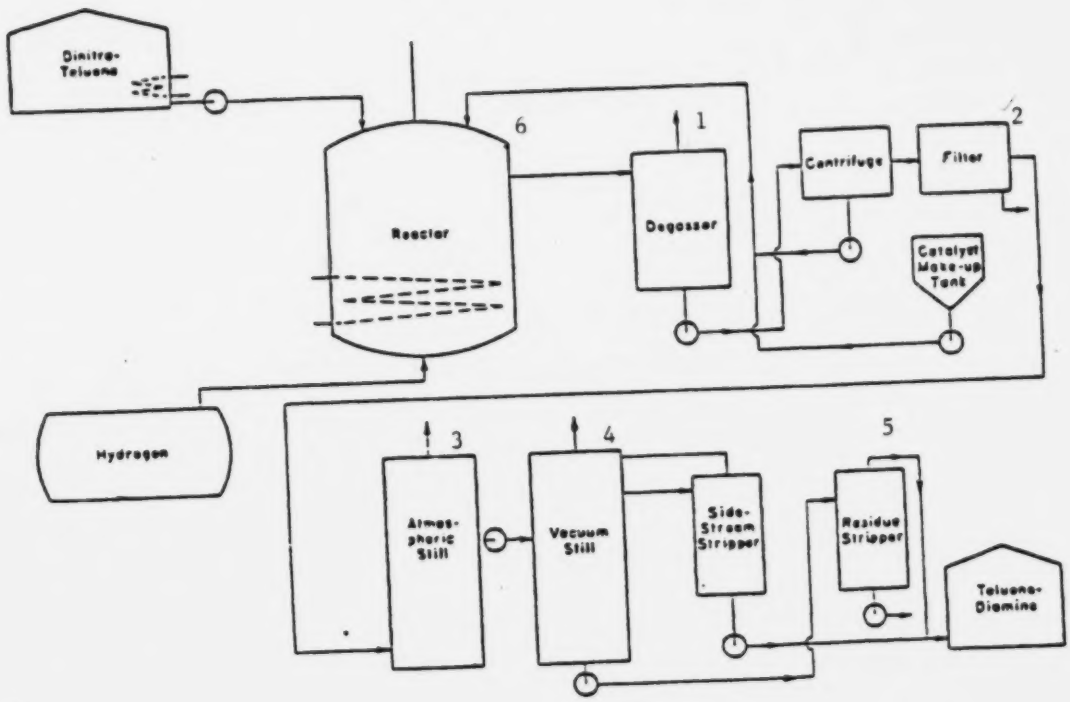
The first general method of 2,4-DAT production is utilized in the manufacture of toluene diisocyanate since this process requires large quantities of 2,4-DAT.

The literature review did not indicate which of the two processes used in the catalytic hydrogenation method is the dominant process nor did the literature suggest what percent of 2,4-DAT is produced by the methods stated above. It is suggested that this should be examined in a phase II materials balance because the method of production and the processes used are major factors in calculating the losses of 2,4-DAT to the environment.

2.1.2 Releases to the Environment During 2,4-Diaminotoluene Production

Figure 2.1 illustrates the production process for 2,4-DAT by the catalytic hydrogenation of dinitrotoluene. No information concerning the details of the production processes were available nor was any information obtained which would indicate the quantities released or the points of release of 2,4-DAT to the environment. Therefore, the diagram in Figure 2.1 was analyzed to determine the points of possible releases of 2,4-DAT. The points numbered in Figure 2.1 correspond to the list of the sources of releases in Table 2.1. There are possible points of release of 2,4-DAT to the environment. A detailed explanation as to the estimated losses at each of these points is discussed in Table 2.1, footnotes 2-6. The largest sources of 2,4-DAT loss during the large scale production process are: Residue from the production process (4300 kkg), catalyst reclamation and disposition of the spent catalyst (1750 kkg), and solvent reclamation and disposition of the spent solvent (900 kkg). These three points of release account for 94 percent of the loss of 2,4-DAT to the environment during the production of 2,4-DAT. The total loss of 2,4-DAT to the environment from the large scale production process is 7,300 kkg. The losses to the different environmental areas are: land-83 percent or 6100 kkg, water-15 percent or 1100 kkg, and air-2 percent or 100 kkg. It should be noted that these estimates are rounded to the nearest ten or hundred. No information was available regarding the losses during the small scale production process. However, the small scale and large scale processes are similar. Solvents and catalysts are used and are sources of releases. Washdown of the equipment as well as spillage are also sources of 2,4-DAT release to the environment.

FIGURE 2.1 PRODUCTION OF 2,4-DIAMINOTOLUENE (Howard et al., 1964)



7,8 - Washdown of processing and storage areas

9,10 - Catalyst and solvent reclamation and disposal

Numbers: Refer to possible sources of release as listed in the Table 2.1 under Point Sources of Releases

TABLE 2.1 RELEASES FROM MANUFACTURE AND IMPORTS

PROCESS	AMOUNT OF 2,4-DAT PRODUCED (kkg)	POINT SOURCES OF RELEASES	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				AIR		LAND		WATER	
				Amt (kkg)	Form	Amt (kkg)	Form	Amt (kkg)	Form
Reduction by H_2 gas using Pd, Pt or Ni catalyst	183,000[1]	• Reactor degasser[2]		7[5]					
		• Disposal of centrifuge filter[2]	60[4] kkg to landfill						
		• Atmospheric still[2]		90[5]					
		• Vacuum still[2]		50[5]					
		• Residue from production process[2]	4300[4] to Landfill						
		• Wastewater from cleaning reactor[2]						60[6]	
		• Washdown of processing areas[2]						100[6]	
		• Washdown of storage area[2]						100[6]	
		• Catalyst reclaiming and deposition of spent catalyst[2]	1750[4] kkg to landfill						
		• Solvent reclaiming and deposition of spent catalyst						900[6]	
Reduction with hydrochloric acid in the presence of an iron catalyst[7]	2100[1,8]	• Deposition of spent solvent[9]						46[10,11]	
		• Deposition of spent catalyst and residues[9]	17[10,12] kkg to landfill						
		• Evaporation and air currents during the production process and storage[9]		2[10,13] vapor and particulate					

TABLE 2.1 RELEASES FROM MANUFACTURE AND IMPORTS (CONTINUED)

PROCESS	AMOUNT OF 2,4-DAT PRODUCED (kkg)	POINT SOURCES OF RELEASES	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				AIR		LAND		WATER	
				Amt (kkg)	Form	Amt (kkg)	Form	Amt (kkg)	Form
		• Washdown of process areas, storage areas, and equipment[9]						1^{3}[10,11]	
		• Washdown of areas due to spillage[9]						7[10,11]	
Imports of 2,4 TDI	0[14]								
2,4-DAT recovery from polyurethane foams	Unknown[15]								
Imports of 2,4-DAT	204[16]	• Spillage, leakage		1[17]				1[17]	
		• Transport		1.5×10^{-3}[19]				1.5×10^{-3}[19]	
Imports of dye	0.3[18]	• Spillage, leakage							
		• Transport							

Table 2.1 Footnote

1. The literature indicated that most of the 2,4-DAT produced was captively consumed. Therefore, the production figures recorded in the International Trade Commission reports did not adequately reflect the true production of 2,4-DAT. The approach used to estimate production was to add the amounts of 2,4-DAT consumptively used to make products and the releases which occurred during these processes. The amounts of 2,4-DAT needed to produce TDI (183,000 kkg) and dyes (2100 kkg) are shown in Table 3.1, footnotes 9 and 13. Estimates of releases during these processes are detailed in Table 3.1 and amount to 31 kkg and 170 kkg respectively. Therefore, 185,300 kkg of 2,4-DAT are needed to produce these products. Amounts of 2,4-DAT available for manufacture of these products come from manufacture of 2,4-DAT and import of 2,4-DAT. Imports of 2,4-DAT amount to 204 kkg and 2 kkg of 2,4-DAT are estimated to be lost during import. Therefore, 202 kkg of 2,4-DAT used in TDI and dye production come from this source. Manufacture of 2,4-DAT must therefore amount to >185,000 kkg of 2,4-DAT.

There are two production processes for 2,4-DAT. Reduction with H_2 gas in the presence of Pt, Pd or Ni catalyst is used for the production of large quantities of 2,4-DAT (Sittig, 1969) whereas reduction with HCl in the presence of iron is a small scale process used mainly in the dye industry (Austin, 1974). Since we had no information on the amounts of 2,4-DAT produced by these two processes, we estimated that the amount of 2,4-DAT used in TDI production (183,000 kkg) would be made by the large scale process and that the remainder of the 2,4-DAT produced (2100 kkg) would be produced by the small scale process.

2. A schematic of the manufacturing process, Figure 2.1, was examined to determine the possible points of release of 2,4-DAT to the environment. The sources of release in this table are in the same sequence as the numbers (one through ten) on the schematic.

3. There was no information in the literature reviewed that stated or indicated the sources of 2,4-DAT release during production nor were any release estimates available. Due to the paucity of information, the following parameters are used to estimate losses during production. The schematic diagram of the 2,4-DAT production process was analyzed for possible points and types of releases. These points and types of releases were ranked according to where the greatest concentration of 2,4-DAT is in relation to points of release.
Based on this process, it was determined that the largest loss to the environment would be to landfills. The residue from the production process, discarded filters, and final deposition of catalyst recovery residues and spent catalyst were estimated to account for 83 percent of the 2,4-DAT lost during production. Losses to air would be primarily from the stills and reactor degasser. The low vapor pressure(1mm Hg at 106.5°C. Weast, 1977) of 2,4-DAT would limit the amount of 2,4-DAT lost to the air. It is estimated that two percent of 2,4-DAT production loss is to the atmosphere. Sources of 2,4-DAT in the waste stream would be via the washdown of production and storage areas, waste water from the cleaning of the reactor and the reclamation or deposition of spent solvent. These wastes would probable enter the municipal waste streams untreated. It is estimated

Table 2.1 Footnote (Continued)

that 1. percent of the 2,4-DAT lost during production would enter the water. From a review of the production process schematic, analysis of similar compound production processes, and number of possible points of releases during production, it is estimated that four percent or 7300 kkg of 2,4-DAT is lost during production.

Based on the preceding information, the following estimates of losses are made (all numbers are rounded):

Release To	Percent Loss	Loss of 2,4-DAT (kkg)
Land	83	6100
Air	2	100
Water	15	1100
		7300

4. The 2,4-DAT losses to landfills during the production process are attributed to residue from production, residue from reclaimed catalyst, deposition of spent catalyst, and disposal of process filters. A review of the production process schematic suggests that a ranking of these possible points of releases based on concentrations and amounts of 2,4-DAT that could be found at these release sites would be in the order stated above. It is therefore estimated that 70 percent (4300 kkg) of the 2,4-DAT lost to landfills is due to the residue from the production process. The reclaimed catalyst residue comprises about 20 percent (1200 kkg) of the 2,4-DAT lost to landfills, and nine percent (550 kkg) is contributed as a result of the final deposition of the spent catalyst. The disposal of filters from the production process yields one percent (60 kkg) loss to landfills.

5. The 2,4-DAT losses to the atmosphere during the production process are considered to be via the atmospheric still, the vacuum still, and the reactor degasser. The production process schematic indicates that the greatest loss would come from the atmospheric still followed by the vacuum still and reactor degasser. Based on this ranking, it is estimated that 60 percent of the air loss (90 kkg) is from the atmospheric still. The vacuum still is thought to account for 33 percent of the loss (50 kkg). It appears that the reactor degasser, because of the recycling of the hydrogen, would only contribute five percent (7 kkg) of 2,4-DAT to the air.

6. The contribution to the water by the liquid waste stream from 2,4-DAT production is thought to be from reclaimed solvent residue and spent solvent deposition, washdown of the storage and production areas due to spillage, general washdown of the processing area, and waste water from the cleaning of the reactor. This ranking was selected as a result of an analysis of the most probable loss sites, the points of greatest concentration of 2,4-DAT and the most likely methods for clean up and disposal.

The greatest contributor of 2,4-DAT to the waste stream is probably the residue from reclaimed solvent which accounts for 60 percent (700 kkg) of the loss to water. It is estimated that the spent solvent which accounts for 15 percent (200 kkg), is deposited in the manufacturing plant's waste stream essentially untreated.

Table 2.1 Footnote (Continued)

The washdown of the processing area and the storage and production areas after 2,4-DAT spillage each represent a 10 percent loss of 2,4-DAT. Therefore, it is estimated that a total of 200 kkg of 2,4-DAT is lost to the plant waste water.

The cleaning of the reactor is estimated to be infrequent. As a result, it is thought that only five percent of the loss of 2,4-DAT attributed to water (60 kkg) occurs from the washdown of the reactor.

7. 2,4-DAT used in the production of dyes is probably all captively consumed and is generally synthesized by the reduction of dinitrotoluene with hydrochloric acid in the presence of a catalyst (Austin, 1974). This method is used because it requires simple equipment (Austin, 1974) and probably produces sufficient quantities of 2,4-DAT for dye production.

8. As was detailed in footnote 1, 2100 kkg of the minimum 185,100 kkg 2,4-DAT produced in the manufacture of 2,4-DAT were estimated to be produced by the small scale process. This estimate is based on the assumption that many dye manufacturers use this process.

9. There is no information in the literature pertaining to the production capacity, the process, or the equipment used in this method of production. An attempt to provide a very rough sketch of the source of possible releases and the quantity of 2,4-DAT lost to the environment is presented. The production process is similar to the process depicted in the production schematic in Figure 2.1. This process uses a solvent and a catalyst. There is probably spillage and washdown of the production area. At some point or points in the process venting must occur. Therefore, these points are considered the primary points of release to the environment during the production cycle.

10. The high solubility in water and the low vapor pressure of 2,4-DAT in combination with the possible points of release are used to suggest a ratio of 2,4-DAT losses to the environment. It is estimated that 78% of the loss is to water, 20% to land, and 2% to air.

The losses of 2,4-DAT during production is estimated to be four percent of the 2,4-DAT produced (84 kkg). Although this process is less sophisticated than the large scale production process in which a four percent loss estimate was calculated, not enough is known about the small scale process to make an estimate. However, it is felt that the loss during production on the small scale process has a high probability of being larger due to its simplicity.

Releases To	Percent Loss	Quantity (kkg) 2,4-DAT Lost
water	78	66
land	20	17
air	2	2

Table 2.1 Footnote (Continued)

11. The 2,4-DAT losses to water occur due to deposition of the spent solvent, washdown of production and storage areas, and washdown of areas due to spillage. It is estimated that the greatest loss, 70 percent (46 kkg) would come from the disposal of the solvent from the manufacturing process because it would have the greatest contact with 2,4-DAT and the separating process probably would not be highly efficient. The washdown of the process, storage and equipment was probably causing a 20 percent (13 kkg) loss of 2,4-DAT. The washdown of an area due to spillage would occur infrequently and the 2,4-DAT lost would probably be small (ten percent or 7 kkg). These 2,4-DAT losses to water would probably go directly to the plant sewer system and leave the plant for the municipal sewer system essentially unmodified.

12. All of the loss of 2,4-DAT to landfills from the production process would occur from the deposition of the spent catalyst and possibly the production residues. It is felt that because of the small scale nature of the production process, these would be mixed together in the plant and form the solid waste. The solid waste from production of 2,4-DAT would contribute 17 kkg of 2,4-DAT to landfills.

13. The vapor pressure of 2,4-DAT is very low even at a high temperature, therefore, the amount of loss would be limited. However, during the production process, it is estimated that there would be opportunities for some evaporation to occur and some particulate matter could be picked up by air currents. As a result, it is estimated that 2 kkg of 2,4-DAT are lost to the air during production and storage.

14. No data on imports of 2,4-TDI could be obtained, so we assumed that none is imported.

15. Since amine recovery from polyurethane forms is a proposed process (Campbell and Meluch, 1977) no information is available on whether it is being implemented, and if so, how much 2,4-DAT is being recovered. According to Campbell and Meluch (1977), approximately 6% of the polyurethanes introduced into the process consist of 2,4-DAT which is recovered. This figure is obtained from a sample run in which 2.4×10^{-3} kkg polyurethanes yields 1.92×10^{-4} kkg 2,4- and 2,6-DAT. This quantity is 8% of the original amount of polyurethane introduced into the system. 75% of this or 6% of the original amount, or 1.45×10^{-4} kkg, is the 2,4-isomer. It may be assumed that if some quantity of polyurethanes undergoes such an operation, then some 6% of it may eventually be yielded as 2,4-DAT.

16. We estimated that approximately 204 kkg 2,4-DAT entered the U.S. as imports in 1977 (USITC, 1978). This value was calculated assuming that 80% of the 4,118 lbs.mixed toluene diamine consisted of 2,4-isomer. This quantity was added to the 446,951 lbs. 2,4-DAT imported and converted to kkg.

17. No data concerning exposure to 2,4-DAT during import of the chemical is available. However, we estimate that a small amount such as 0.5% or 1 kkg each might be lost to air and water. This may occur due to spillage, leakage and breakage during shipping and handling.

Table 2.1 Footnote (Continued)

18. We estimate that about 0.3 kkg 2,4-DAT was found in dyes imported into the U.S. in 1977. This value was found from totaling the number of kkgs of 2,4-DAT dyes imported (see Table 3.5), which yielded a quantity of 5.22 kkg. Approximately 5% of the dye (0.3 kkg) may be 2,4-DAT (see footnote 18, Table 3.1 for further explanation).

19. About 1% of the amount imported (0.3 kkg) might be released due to spillage, leakage, or breakage during shipping and handling. This approximates 0.5%, or 1.5×10^{-3} kkg, 2,4-DAT lost to air and a similar amount to water.

There are five possible points for release of 2,4-DAT to the environment. A detailed explanation as to the estimated losses at each of these points is presented in Table 2.1, footnotes 8-13. The primary sources of 2,4-DAT loss during production include: Final disposition of the spent solvent (46 kkg), disposal of the spent catalyst and residues (17 kkg), and the washdown of the equipment and storage areas (13 kkg). These three sources of 2,4-DAT releases during the production process contribute 89 percent (76 kkg) of the 2,4-DAT releases to the environment.

The total loss of 2,4-DAT to the environment during this production process amounts to 85 kkg. This figure is divided among the three pathways in the following proportions: water-78 percent or 66 kkg, land-20 percent or 17 kkg, and air-2 percent or 2 kkg. These estimates represent values rounded to the nearest whole number.

2.1.3 Producers

The literature reviewed did not state the production capacity of any plant nor the estimated average production of the manufacturing plants. Attempts to obtain information from industry about production capacities of a typical 2,4-DAT plant were unsuccessful.

The Directory of Chemical Producers (1977) did state that nine companies at 15 locations produced 2,4-DAT. The greatest geographical concentration of manufacturers is in West Virginia which contained six manufacturing plants (Figure 2.2). Four of these manufacturing sites are in two cities - Institute, West Virginia and South Charleston, West Virginia.

There are two other geographical areas in which 2,4-DAT manufacturing appears to be concentrated: The Gulf Coast contains four sites in two states - Texas and Louisiana, and New Jersey contains two sites.

2.2 RELEASES FROM IMPORTS OF 2,4-DIAMINOTOLUENE

We estimate that about 204 kkg of 2,4-DAT was imported into the U.S. in 1977 (United States International Trade Commission, 1978). (See Table 2.1, footnote 16). No information concerning exposure to the compound due to imports was located, but it may be assumed that release was probably rather minimal. Therefore, an estimate of some small amount such as 0.5% each to air and water (1 kkg each) may be used.

FIGURE 2.2 PRODUCERS OF 2,4-DIAMINOTOLUENE
(Directory of Chemical Producers, 1977)

Air Products and Chemicals, Inc.	Pasadena, TX
Allied Chemical Corporation Specialty Chemicals Division	Moundsville, WV
American Cyanamid Company Organic Chemicals Division	Bound Brook, NJ
E.I. duPont de Nemours & Co., Inc. Organic Chemicals Department, Dyes and Chemicals Division	Deepwater, NJ
GAF Corporation Chemical Products	Rensselar, NY
Mobay Chemical Corporation Industrial Chemicals Division Polyurethane Division	New Martinsville, WV Cedar Bayou, TX
Olin Corporation Agricultural Products Division Designed Products Division	Lake Charles, LA Brandenburg, KY Rochester, NY Geismar, LA
Rubicon Chemicals, Inc.	Institute, WV South Charleston, WV
Union Carbide Corporation Chemicals and Plastics Division	Institute, WV South Charleston, WV

2.3 RELEASES FROM AMINE RECOVERY FROM POLYURETHANE FOAMS

In 1977, General Motors Corporation described a process by which 2,4- and 2,6-DAT could be recovered from polyurethane foam (Campbell and Meluch, 1977). As tested, the operation recovered approximately 6% of the total amount of polyurethane foam introduced into the system as 2,4-DAT. No information is available, however, as to whether or not this process is being used. Therefore, no real estimates can be made concerning how much 2,4-DAT is made via this operation.

2.4 RELEASES FROM IMPORTS OF 2,4-TOLUENE DIISOCYANATE

No information was available concerning imports of 2,4-TDI or whether 2,4-TDI is imported.

2.5 RELEASES FROM IMPORTS OF DYES

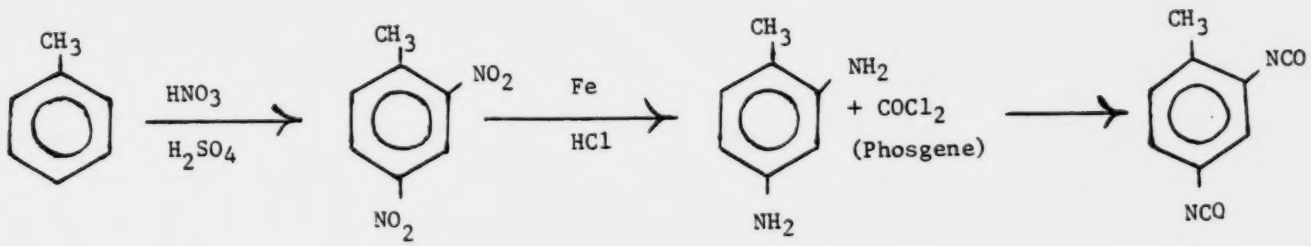
We estimated that about 0.3 kkg 2,4-DAT is found as a contaminant of the 2,4-DAT dyes imported into the U.S. (See Table 2.1, footnote 18). Of this quantity, we then assumed that a minute amount such as 0.5% each might be lost to land and to water. This equals about 1.5×10^{-3} kkg 2,4-DAT released into air and the same amount into the water.

3.0 RELEASES FROM USES OF 2,4-DIAMINOTOLUENE

3.1 RELEASES FROM PRODUCTION OF 2,4-TOLUENE DIISOCYANATE

2,4-DAT finds it major use in the production of 2,4-toluene diisocyanate (TDI) which is in turn utilized in the production of polyurethane foams.

TDI is a colorless liquid which is synthesized from 2,4-DAT and phosgene. The reaction sequence, beginning with toluene, is as follows (Phillips and Parker):



toluene — 2,4-dinitro-toluene — 2,4-diamino-toluene — toluene diisocyanate

The physical properties of TDI are detailed in Appendix B.

Most of the 2,4-DAT produced is employed in the preparation of 2,4-TDI; a small percentage goes to dye manufacture (Chemical Market Abstracts, 1977). We estimate that approximately 183,000 kkg 2,4-DAT is used in the production of 229,000 kkg 2,4-TDI (Table 3.1, footnote 1).

A map of the producers of TDI and their capacities are shown in Figure 3.1.

An examination of the sources of release of 2,4-DAT during 2,4-TDI manufacture follows. Table 3.1 provides a detailed summary of the amount of these releases and how these estimates were derived.

During the 2,4-TDI manufacturing process, there are several potential points for release of 2,4-DAT into the environment (Figure 3.2). The first is during the initial introduction of 2,4-DAT into the first reactor with phosgene (Processes Research, 1977). Since this is a closed system, the possibility of spillage or leakage of the phosgenaters is small, and therefore,

TABLE 3.1 RELEASES DURING USES OF 2,4-DIAMINOTOLUENE

PROCESS	AMOUNT OF 2,4-DAT USED (kkg)	PT. SOURCES OF RELEASES	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt (kkg)	Form	Amt (kkg)	Form	Amt (kkg)	Form
Production of 2,4 TDI	183,000[1]	• leaks in pipeline to feed 2,4-DAT into phosgenators		negligible[2]	free				
		• HCl and phosgene solvent recovery		negligible[3]	free				
		• leaks in pipeline containing 2,4-TDI							
		• residue from fractionating column (incinerated or landfilled)	6.5[4]	0.3[5]	free				
		• losses to air vents & scrubber system		1[6]				17[6]	
		• transport							
		• storage							
		• disposal							
Uses of TDI									
Production of Foams	925[7] as a contaminant	• Leakage or spills of TDI at introduction to foam manufacturing machinery							

TABLE 3.1 RELEASES DURING USES OF 2,4-DIAMINOTOLUENE (CONTINUED)

PROCESS	AMOUNT OF 2,4-DAT USED (kkg)	PT. SOURCES OF RELEASES	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt (kkg)	Form	Amt (kkg)	Form	Amt (kkg)	Form
		• loss of 2,4-DAT from foam due to exotherm and CO_2 production • amounts of 2,4-DAT remaining in foam molds		$\geq 5 \times 10^{-5}$ [10] (negligible)	free				
Production of Other Polyurethane Products	80[7] as a contaminant	• leakage or spills of TDI at introduction to process • losses through ventilation system		$\leq 4 \times 10^{-6}$ [9] (resins) negligible	free			negligible[9] (resins)	
Export	135[7] as a contaminant	• losses, during transport from country		2[11]	free	1[11]	free		
Use of Polyurethane Products									
Foams	925[8] as a contaminant	• losses of 2,4-DAT contaminants in foam during use	65[12] stored in foams	≤ 1[12]	free				

TABLE 3.1 RELEASES DURING USES OF 2,4-DIAMINOTOLUENE (CONTINUED)

PROCESS	AMOUNT OF 2,4-DAT USED (kkg)	PT. SOURCES OF RELEASES	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt (kkg)	Form	Amt (kkg)	Form	Amt (kkg)	Form
Other	80[8] as a contaminant	• losses of 2,4-DAT from other polyurethanes during use							
Manufacture of Dyes	2100[13]	• Liquid waste stream from the manufacturing and cleanup of the dye production						150[14]	Dissolved or Suspended in Water
		• Solid wastes from the distillation and filtering of residues before release to the municipal waste stream	20[14] to landfill						
		• Vapor and particulate from the evaporation of water during the drying and pressing process of dye manufacture		2[14]	vapor and particulate matter				

TABLE 3.1 RELEASES DURING USES OF 2,4-DIAMINOTOLUENE (CONTINUED)

PROCESS	AMOUNT OF 2,4-DAT USED (kkg)	PT. SOURCES OF RELEASES	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				Air		Land		Water	
				Amt (kkg)	Form	Amt (kkg)	Form	Amt (kkg)	Form
Usage DYE - Leather and Textile (840kkg)[15]	40[18] as a contaminant	• Waste water from the dyeing process sent to municipal sewer after filtering	4[19] to landfill					36[19]	liquid and attached to solid
Hair Dyes (5kkg)[16]	5[18]	• Application to hair and waste stream sent to municipal sewer	0.05[20] kkg absorbed by the skin					0.2[20]	liquid
Uses of Other Dyes (1250kkg)[17]	60[18] as a contaminant	• Probably sent to municipal sewers after filtering	6[21] to landfill					54[21]	liquid
Dye Developer	unknown	• Wastewater from dyeing process sent to municipal sewer after filtering							

Table 3.1 Footnote

1. Production figures for TDI for 1977 were reported by the U. S. International Trade Commission to be approximately 265,000 kkg (80% 2,4-isomer and 20% 2,6-isomer). In addition, we estimate that about 26,500 kkg TDI (65% 2,4-isomer and 35% 2,6-isomer) may have been produced since small amounts of this mixture are also used in polyurethane production; we were, however, unable to obtain data on its production. Amounts of 2,4-TDI in these mixtures are estimated to be 265,000 kkg (0.8) + 26,500 kkg (0.65) = 229,000 kkg. In order to produce this quantity of 2,4-TDI, 183,000 kkg 2,4-DAT would be required. This estimate is based upon a yield of 1 g. 2,4-TDI from approximately 0.8 g 2,4-DAT; the 0.8 g needed is derived from an average of 0.72 g (Processes Research, 1977) and 0.88 g (Faith et al., 1975) cited for this process.
2. Since a closed system is used for 2,4-TDI manufacture, release of 2,4-DAT due to leaks are probably negligible; in addition 2,4-DAT has a low vapor pressure (Weast, 1977) and would not readily volatilize.
3. This amount is negligible due to the low vapor pressure of 2,4-DAT.
4. Processes Research states that 0.00058 kkg of waste isocyanates/kkg TDI produced is present in the centrifuge residue from TDI manufacture. Since 229,000 kkg of 2,4-TDI are estimated to have been produced in 1977 (footnote 1), waste isocyanates in the centrifuge residue are estimated to be 133 kkg. If we assume that 10% as much 2,4-DAT may be present in these wastes, we would estimate that 13 kkg of 2,4-DAT is present.

Centrifuge residue wastes appear to be disposed of in two ways: landfilling (Processes Research, 1977) and incineration (Kirk-Othmer, 1969). We estimate that 50% might be landfilled (6.5 kkg).
5. If 50% of the centrifuge residue (footnote 4) is incinerated, this amount would equal 6.5 kkg. We estimate that during incineration, approximately 5% may be lost to air (0.3 kkg).

6. Losses of 2,4-DAT to air vents during TDI production was estimated at 0.01% due to the low vapor pressure of 2,4-DAT and the fact that a large portion of 2,4-DAT has been consumed in the reaction. This amounts to 18 kkg. Of this amount, about 95% is probably trapped in the scrubber water on these vents (17 kkg) while a remaining 1 kkg would be released to air. This estimate is based on the high water solubility of 2,4-DAT.
7. Amounts of 2,4-TDI used in the production of polyurethane foams (81%), other urethane products (7%) and 2,4-TDI exports (12%) were estimated utilizing percentages found in Faith, et.al. (1975). These quantities were 185,000 kkg, 16,000 kkg, and 27,000, respectively. Since 2,4-TDI has a minimum purity of 99.5% (Kirk-Othmer, 1969), the maximum amount of 2,4-DAT in 2,4-TDI is 0.5%. This percentage was used to obtain the maximum amounts of 2,4-DAT which could enter polyurethane foams as an impurity.
8. Since losses of 2,4-DAT during polyurethane production appear to be negligible, amounts of 2,4-DAT entering polyurethane use are the same as those entering polyurethane production.
9. To estimate the amounts of polyurethanes produced in the United States, we used the world production figure for polyurethanes (5300 million lbs.) (Threlkeld, 1977) and multiplied by 0.40 since 40% of that figure was U. S. demand (Threlkeld, 1977). This amount was 962,000 kkg. Approximately 60% of this amount is TDI polyurethanes (Chemical Market Abstracts, May 1977) based upon 405 million tons of TDI used/680 tons of isocyanates.

Table 3.1 Footnote (Continued)

Therefore, 577,000 kkg of TDI polyurethanes are manufactured per year. Using percentages of TDI use in polyurethane manufacture obtained from Faith et. al. (1975), the following amounts of TDI polyurethane products are produced:

Foams (81%/88% = 92%) = 531,000 kkg

Other Urethanes (including resins) (7%/88% = 8%) = 46,000 kkg

To calculate the amount of 2,4-DAT released, we obtained the amount of TDI released at 1.8×10^{-8} kkg/kkg resin (Midwest Research Institute, 1974) assuming 100% of "other urethanes" was resins. This amount was 8×10^{-4} kkg. Amounts of 2,4-DAT released would be approximately 0.5% of TDI (based on purity of TDI in Kirk-Othmer, 1969) = 4×10^{-6} kkg. In addition a negligible amount of 2,4-DAT would be released to waste water through scrubbers on the ventilation system.

10. To obtain amounts of 2,4-DAT released during foam production, we assumed that greater amounts would be released than are released during resin production (1.8×10^{-8} kkg/kkg resin) (Midwest Research Institute, 1974). This assumption was based upon the fact that foam production is an exothermic reaction which evolves gas (CO_2). Using the same calculation as in footnote 8, we calculated TDI loss as $\geq 10 \times 10^{-3}$ kkg and 2,4-DAT release as $\geq 5 \times 10^{-5}$ kkg.

11. The amount of DAT exported with TDI was calculated at 135 kkg (footnote 7). Of this we estimated that 2% might be lost during export from the country totalling 3 kkg. Of this we estimate that 2 kkg would be released to air through evaporation and 1 kkg would be released to water due to spills.

12. Guthrie and McKinney calculated an average of 125 ppm 2,4-DAT in polyurethane foams. Using this average and the amount of TDI polyurethane foams produced (footnote 8), we calculate 66 kkg of 2,4-DAT in foams. From this we estimated that 2% might be emitted through volatilization (1 kkg). The rest would remain in foams (65 kkg).

13. Dyes produced from 2,4-DAT were obtained from the Colour Index (1971). Using International Trade Commission reports, an estimate of the maximum amounts of 2,4-DAT used in the production of 2,4-DAT dyes was obtained. The amounts of 2,4-DAT dyes produced during 1974-1977 are shown in Table 3.5. Due to the absence of data in the ITC reports, we estimated the amount of dye which was produced from 2,4-DAT by using amounts stated in these reports for specific dyes and any amounts found in appropriate categories, such as "all other direct brown dyes". However, not all 2,4-DAT dyes are produced in the United States each year (World Health Organization, 1978) so some categories may be included when no dyes in those categories were actually produced. The totals of the dye categories are shown in Table 3.5. Since sulfur dyes appeared under the category "all other dyes" we used both 10% and 100% of the amounts in these categories. These totals amounted to 5.5 - 13.1% of the total dye production for 1977. As a maximum estimate of the percentage of dyes which were produced from 2,4-DAT in 1977, we chose 6%.

Using 120,000 kkg production of dyes in 1977, a maximum of 7200 kkg of 2,4-DAT dyes would have been produced. From the formulation of 13 of the 2,4-DAT dyes, it was estimated that 29% of the dye composition was due to 2,4-DAT. Therefore, we estimated that 2100 kkg of 2,4-DAT would have been used in the production of 7200 kkg of 2,4-DAT dyes.

Table 3.1 Footnote (Continued)

14. During the manufacture of 2,4-DAT dyes it is estimated that eight percent of the 2,4-DAT used in the production of the dyes is lost to the environment. A review of the literature yielded no quantitative assessment of the loss of 2,4-DAT during dye production. However, the literature in general indicated that the production of dyes is a simple process with minimal production and quality control guidance.

During dye production, the loss of 2,4-DAT to the environment is calculated to be approximately 170 kkg. The dye industry releases 2,4-DAT to air, land, and water (Industrial Process Profile for Environmental Use on the Organic Dyes and Pigment Industry, 1977). Loss to the environment is greatest to water, land, and air, in that order. It is therefore, estimated that 90% 2,4-DAT is released to water, 9.99% to landfill and .01% to air.

15. Approximately 3180 kkg dyes are utilized by the leather industry (Radding et. al., 1978). It has been estimated that 6% of the dyes employed are 2,4-DAT dyes (see footnote 13). This yields about 200 kkg 2,4 DAT to be used in the leather industry in 1977. Approximately 45,454 kkg of dye are consumed by the textile industry each year (Jones,1973); if 6% of these dyes are in part synthesized from 2,4-DAT, then 2700 kkg 2,4-DAT dyes are consumed in this industry. The total quantity of 2,4-DAT based dyes used in these industries is 2900 kkg. Based on dye formulas about 29% of the dye is composed of 2,4-DAT. Therefore, 840 kkg 2,4-DAT is consumed in dye production.

16. Twenty million people dyed their hair in 1975. Seventy-five percent of the hair dyes are oxidative hair dyes and there is 60 mg of 2,4-DAT in the hair dye (Ames et al., 1975). If each person dyes their hair six times a year, then 5 kkg of 2.4-DAT are used in hair dyeing operations.

17. The textile, leather and hair products industries consume approximately 845 kkg of the 2100 kkg 2,4-DAT used in the preparation of dyes or in dyeing operations. About 1250 kkg 2,4-DAT is used for other types of dyes which include stains, dyes, indicators, silk screen inks and pigments. No data was available that could be used to determine the amounts of 2,4-DAT used for production of each of these types of dyes.

18. It is estimated that 5% of the 2,4-DAT used to manufacture dyes remains in the dye as an impurity based on the fact that an excess of 2,4-DAT would be required in some reactions and the fact that the dye does not appear to be separated from the reactants subsequent to the reaction. It is estimated that 840 kkg of 2,4-DAT is consumed in production of leather and textile dyes (see footnote 15). Then about 40 kkg 2,4-DAT may be passed along as dye contaminant into dyeing operations.

Other types of dyes consume about 1250 kkg 2,4-DAT. If 5% of this quantity is a contaminant, then about 60 kkg 2,4-DAT is sent forth to dyeing operations.

19. About 90% of the 2,4-DAT contaminate in dyes is estimated to be lost to the waste stream and 10% to the residue from the dyeing process. This ratio is based on information obtained from the literature indicating that the dyeing process is a batch process taking place in large, partially open vats. The dyeing process occurs in these vats; subsequent to their use, the dyes are subjected to some type of filtering process, and then released into municipal sewer systems (Radding et.al, 1978). All of the 2,4-DAT contaminant is probably dissolved or

Table 3.1 Footnote (Continued)

suspended in the dye solution. Since 2,4-DAT is a contaminant, it may not react in the dyeing process. If it does react, the amount which would react is estimated to be low. As a result, 2,4-DAT probably does not enter into the reactions taking place during dyeing to any significant degree, and is most likely released en masse to the wastewater effluent.

About 90% of the 40 kkg 2,4-DAT used in leather and textile dyes is released to the environment via wastewater - about 36 kkg. The remaining 10%, or 4 kkg, is lost in the residue from the filtering of the waste stream, and is landfilled.

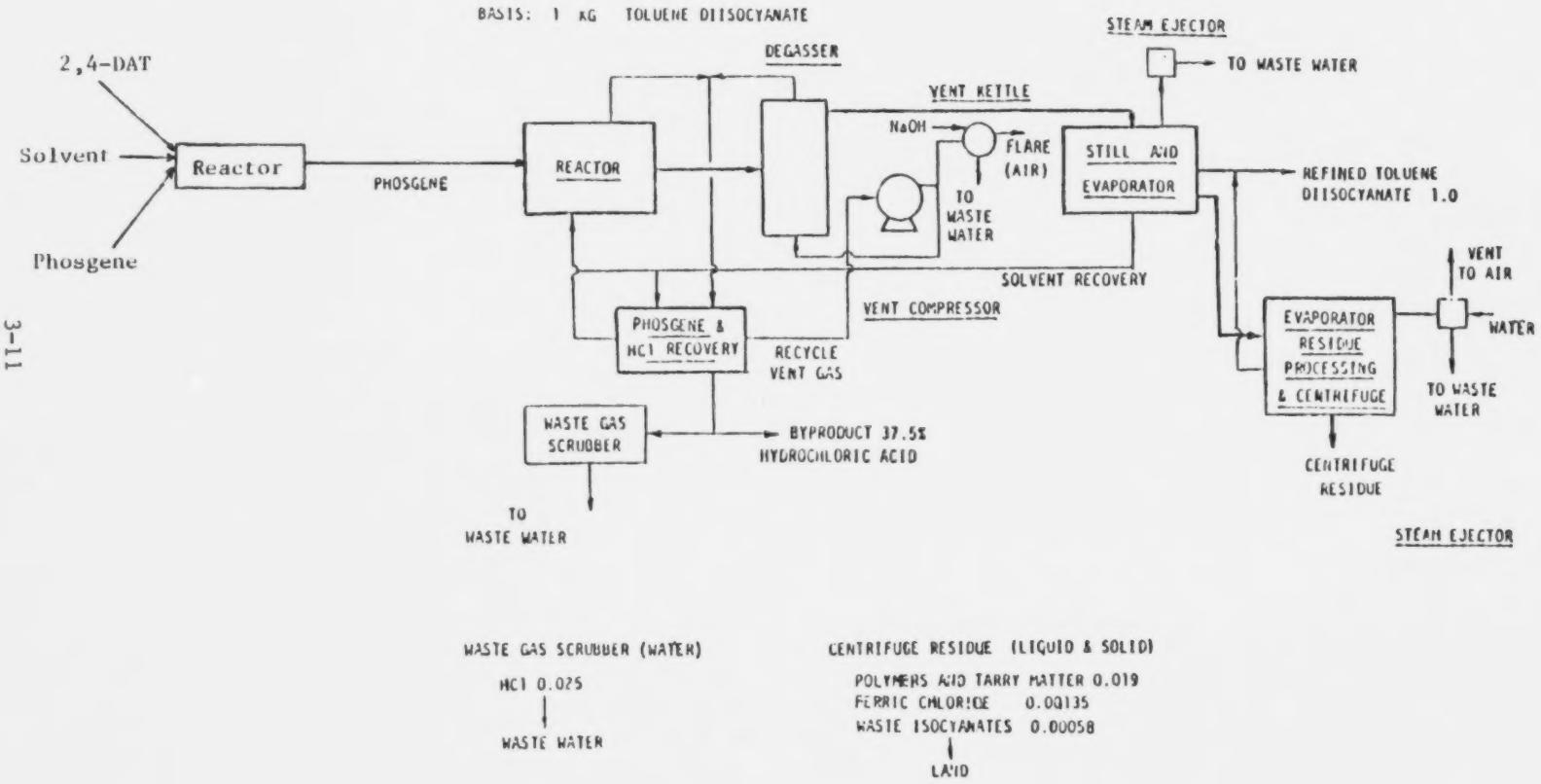
20. The process of hair dyeing requires the consumer to wet the hair, apply the coloring agent and developer, wait for a prescribed time period, and then rinse the hair. One percent of the chemicals will be absorbed by the scalp (Ames et al., 1975). The coloring agent and developer will react to form the dye. Assuming that 95% of the 2,4-DAT reacts, 4% will remain unreacted and will enter the municipal sewer system during the rinsing.

21. Footnote 18 delineates the calculations used to obtain amounts of release of 2,4-DAT from the use of other types of dyes. Approximately 90% of the 60 kkg used for such dyes is released to wastewater (54 kkg), and 10%, disposed of in landfill.

FIGURE 3.1 PRODUCERS OF TOLUENE DIISOCYANATE (Gunn and Cooke, 1976)

		Annual Capacity (kkg)
Allied Chemical Corporation Special Chemicals Division	Moundsville, WV	36,000
BASF Wyandotte Corporation Industrial Chemicals Group	Geismar, LA	25,000
E.I. du Pont De Nemours & Co., Inc. Elastomer Chemicals Department	Deepwater, NJ	48,000
Dow Chemical Company	Freeport, TX	46,000
Mobay Chemical Corporation	Cedar Bayou, TX	57,000
Industrial Chemicals Division	New Martinsville, WV	45,000
Olin Corporation		
Agricultural Chemicals Division	Lake Charles, LA	41,000
Designed Products Division	Ashtabula, OH	18,000
Rubicon Chemicals, Inc.	Geismar, LA	18,000
Union Carbide Corporation Chemicals and Plastics Div.	Institute, WV S. Charleston, WV	25,000
	Total	358,000

FIGURE 3.2. TOLUENE DIISOCYANATE MANUFACTURE (Processes Research, 1977)



the amount of 2,4-DAT released is negligible. Any that is released would, it is assumed, volatilize into the air.

A slurry resulting from the reactions of phosgene and 2,4-DAT is pumped to a second reactor, where it further reacts with gaseous phosgene. Liberated hydrogen chloride and any unreacted phosgene leave the reactor to go through a recovery system in order to recycle the gases. Gas scrubbers are used for this purpose and to prevent the gases from escaping into the atmosphere. It is likely that some amount of 2,4-TDI and of 2,4-DAT is present in the waste gas mixture, but due to the low vapor pressure of 2,4-DAT, it is probably negligible (Processes Research, 1977).

The third reaction vessel is the site of conversion to 2,4-TDI. An inert gas is blown through the system, and the resulting crude TDI is sent to a still and evaporator for purification. The evaporator residue is processed and centrifuged. This is the third site of possible 2,4-DAT contamination (Processes Research, 1977). As explained in Table 3.1 (footnotes 4 & 5), it is estimated that 6.5 kkg 2,4-DAT is landfilled every year and that 0.3 kkg is released into the air.

Leaks in the pipeline which transport 2,4-TDI along the processing operation are also potential sources of release, but no data is available for this. It is assumed, however, that these releases would be negligible.

There are several points in the manufacturing process where waste is shunted into wastewater disposal. An estimate of about 17 kkg 2,4-DAT is likely to be released into the environment via wastewater effluent, whereas 1 kkg may be lost to the air by venting.

Other sources of 2,4-DAT exposure could be in disposal or storage of 2,4-TDI and in transport of 2,4-TDI to polyurethane manufacture. However, it is difficult to make any estimation of release since no data is available.

3.2 RELEASES FROM USES OF TOLUENE DIISOCYANATE

TDI is used primarily in the production of such diverse articles as foam-type mattresses and polyurethane products, enamelled wire, inks and adhesives (Chemical Market Abstracts, 1977) (Tables 3.2 and 3.3).

TABLE 3.2 ALTERNATE USES OF TOLUENE DIISOCYANATE IN 1976 AND 1977, IN PERCENT AND KKG (CHEMICAL MARKET ABSTRACTS, 1977)

		Flexible and Semi-Rigid Urethane Foam	Polyurethane Coatings	Elastomers	Others
Percent		90	5	3	2
Amount	1976	228,000	13,000	8000	5000
	1977	249,000	14,000	8000	5000

TABLE 3.3 1975 U.S. RIGID URETHANE FOAM MARKET IN PERCENT AND KKG FOAM (CHEMICAL MARKET ABSTRACTS, 1977)

	Percent	Foam (kkg)
Construction	39.1	60,000
Tank & Pipe	12.9	20,000
Appliances	20.6	32,000
Transportation	10.6	16,000
Furniture	5.9	9,000
Marine Flotation	2.9	5,000
Packaging	3.5	5,000
Miscellaneous	4.5	7,000
Total	100.0	154,000

Several types of urethanes can be made. Among the kinds of urethanes produced are flexible and rigid foams, which account for approximately 90% of urethane manufacture, and coatings, adhesives and cast elastomers, which comprise the remaining 10% of polyurethanes (World Health Organization, 1978).

3.2.1 Releases from Production of Polyurethane Foam Products

Polyurethane foams are produced by a reaction of TDI with polyesters of dicarboxylic acid, such as adipic acid, and glycol or glycerine. Catalysts for the reaction include cobalt naphthenate, organotin compounds and various amines. If the polyester contains a free hydroxyl group and carboxyl group, the isocyanate will react with the carboxyl to produce carboxamide linkages. Carbon dioxide is produced simultaneously with the latter reaction. The reacting mass becomes very tough and traps the carbon dioxide; it swells into a strong, rigid but light foam. The foams are poured or sprayed into position where the final cure occurs (Lowenheim and Moran, 1975).

Urethane cellular foam products are produced from pure TDI and treated still bottoms containing dimers and trimers of TDI. TDI plus polyether and water can be reacted together to produce flexible urethane foams; these are used for furniture cushions, mattresses and automotive seating. Cellular polyester foams are made from TDI and polyester adipate resin. These foams are employed in the textile trade for heat lamination of this gauze foam sheeting to a variety of fabrics. Rigid urethane foams, which are synthesized from TDI and polyhydroxyl polyethers blown with monofluorotrichloromethane, are utilized in insulation (e.g., transportation equipment, home construction panels, industrial appliances, refrigerators, packaging, etc.) (Simonds, and Church, 1967).

During manufacture of polyurethane foams from 2,4-TDI, several points of exposure to 2,4-DAT have been identified (see Table 3.1).

We have estimated that about 925 kkg 2,4-DAT is contained in the 2,4-TDI used to produce 531,000 kkg foams yearly.

Leakage or spills of 2,4-TDI at the introduction of this compound to the polyurethane manufacturing process is a potential source of release of 2,4-DAT

however, no data on this exposure is available in order to make estimates. In addition, 2,4-DAT is likely to be found in residue left in foam molds and in releases from disposal and storage but again, no data on this could be located.

An estimate of release of greater than 5×10^{-5} kkg 2,4-DAT was obtained, however, for the exothermic part of the reaction in which carbon dioxide is produced (Smith and LaShelle, 1974) (see Table 3.1, footnote 10). Although this quantity is negligible, it is assumed to be greater than amounts released in resin facilities since the foams are produced under exothermic conditions and gas is evolved. This quantity would be released into the air as free 2,4-DAT.

3.2.2 Releases from Production of Other Polyurethane Products

Urethane coatings are prepared from polyols and TDI. These are made from any ratio or combination of urethane linkages, active isocyanate groups or polyisocyanate monomers (Simonds and Church, 1967).

TDI and polyhydroxy compounds can be employed to form urethane elastomers, long linear polyurethanes (Simonds and Church, 1967).

Finally, spandex fibers are made from polyurethane. These fibers contain at least 85% segmented urethane. These are used in hosiery, swimsuits, foundation garments and related products (Simonds and Church 1967).

An estimate of 80 kkg 2,4-DAT is contained in the amount of 2,4-TDI used to produce 46,000 kkg polyurethanes other than foams. Very little industrial process information was found, although it is assumed that releases of 2,4-DAT may occur at points such as leakage or spills of 2,4-TDI at the beginning of manufacture (although this quantity would likely be negligible), and losses during transport.

An estimate of less than 4×10^{-6} kkg 2,4-DAT can be assumed to be released to the air in the manufacturing of polyurethanes other than foams. This quantity would probably be released via ventilation systems and can be considered negligible. In addition, a very minimal amount of 2,4-DAT is probably lost in the wastewater effluent from these plants.

3.2.3 Releases from Export of Toluene Diisocyanate

Approximately 135 kkg 2,4-DAT is a contaminant in the 2,4-TDI exported from the U.S. (see Table 3.1). About 2 kkg may be released to the air and 1 kkg to water.

3.3 RELEASES FROM USE OF POLYURETHANE PRODUCTS

3.3.1 Releases from Use of Polyurethane Foam

It has been determined that a certain amount of 2,4-DAT contamination exists in polyurethane foams (Guthrie and McKinney, 1977). This is due either to hydrolysis of 2,4-DAT or to a 2,4-DAT impurity or to both. As shown in Table 3.4, Guthrie and McKinney tested 11 different commercial foams for their 2,4-DAT content. From this, an estimate of 125 ppm 2,4-DAT was obtained. This led to an approximation of 65 kkg 2,4-DAT stored in foams which will eventually be landfilled, and some quantity less than 1 kkg which is released to the air (see Table 3.1, footnote 12).

3.3.2 Releases from Use of Other Polyurethane Products

It is assumed that 2,4-DAT is a contaminant in other polyurethane products to some degree, and that some quantity of it is released. However, no data on its release is available, so it is difficult to estimate what amount would be released to the environment. Since only 80 kkg 2,4-DAT is used in the production of non-foam polyurethanes relative to the 925 kkg employed in foam manufacture, the amounts released would be expected to be much lower.

3.4 RELEASES FROM DYE PRODUCTION

Over 91,000 kkg of organic dyes are produced in the United States each year (U.S. International Trade Comission). As an intermediate, 2,4-DAT is used in the production of basic, direct, solvent, mordant, and sulfur dyes. Table 3.5 lists those dyes made from 2,4-DAT.

Dyes produced from 2,4-DAT constitute a small portion of the organic dyes. Between 1974 and 1977, 2,4-DAT dyes probably comprised less than 6 percent of the dyes produced (see Table 3.6); this represented more than 5400 kkg of dye each year.

TABLE 3.4 2,4-DIAMINOTOLUENE CONTENT OF FLEXIBLE POLYURETHANE FOAMS (Guthrie and McKinney, 1977)

Foam No.	Type	2,4-DAT Concentration (ppm)
1	Hydrophilic Polyether, Type 1	20
2	Hydrophilic Polyether, Type 2	77
3	Hydrophilic Polyether, Type 3	6
4	Hydrophobic Polyether, Type 1	67
5	Hydrophobic Polyether, Type 2	338
6	Hydrophobic Polyether, Type 3	99
7	Hydrophobic Polyether, Type 4	123
8	Hydrophilic Polyester, Very Old	20
9	Hydrophilic Polyester, Fresh	112
9	Hydrophilic Polyester, Fresh	442
10	Hydrophobic Polyester, Type 1	27
11	Hydrophobic Polyester, Type 2	19
11	Hydrophobic Polyester, Type 2	52

Reproduced from best available copy.

TABLE 3.5 DYES PRODUCED FROM 2,4-DIAMINOTOLUENE

TABLE 3.5 DYES PRODUCED FROM 2,4-DAT

C.I. NUMBER	C.I. NAME	1974				1975				1976				1977				1978
		PRODUCTION (U.S.) (kg)	SALES (U.S) (kg)	IMPORTS (kg)	MANUFACTURERS (U.S.)	PRODUCTION (U.S.) (kg)	SALES (U.S) (kg)	IMPORTS (kg)	MANUFACTURERS (U.S.)	PRODUCTION (U.S.) (kg)	SALES (U.S) (kg)	IMPORTS (kg)	MANUFACTURERS (U.S.)	PRODUCTION (U.S.) (kg)	SALES (U.S) (kg)	IMPORTS (kg)	MANUFACTURERS (U.S.)	IMPORTS (kg)
11320	C.I. BASIC ORANGE 1	132	174.2		ACS,ACY,CAP,PSC, TBC	- - - -	- - - -		ACS,ACY,CAP,PSC, TBC	- - - -	- - - -		ACS,ACY,CAP,PSC, TBC	- - - -	- - - -		PSC,TBC	
11320.1	C.I. SOLVENT ORANGE 4																	
11325	BASIC DYE																	
11330	C.I. SOLVENT BROWN 2																	
11335	C.I. MORDANT BROWN 4																	
13320	C.I. DIRECT BROWN 53																	
20140	DIRECT DYE (COTTON BROWN BH)																	
21010	C.I. BASIC BROWN 4	215	219	0.05	ACS,ACY,DSC,DUP, CAP,PSC,TBC	96	139	0.05	ACS,ACY,DSC,DUP, CAP,PSC,TBC	- - - -	- - - -	2	ACS,ACY,CAP,PSC, TBC	- - - -	- - - -	5	CAP,PSC,TBC	1
21010.1	C.I. SOLVENT BROWN 12	9	8		DSC,CAP,PSC	- - - -	- - - -		ACS,DSC,CAP,PSC	- - - -	- - - -		ACY,CAP,PSC	- - - -	- - - -		PSC	
21010.2	C.I. PIGMENT BROWN 3	- - - -	- - - -		KON,KON	- - - -	- - - -		KON,KON	- - - -	- - - -		KON,KON	- - - -	- - - -		KON	
24080	C.I. DIRECT VIOLET 13																	
25070	DIRECT DYE (DIPHENYL FAST BLACK)																	
30010	DIRECT DYE (NAPHTHAMINE DIRECT BROWN BR)																	
30020	DIRECT DYE (NAPHTHAMINE FAST BLACK SE)																	
30100	C.I. DIRECT BROWN 17																	
30105	DIRECT DYE (DIAMINE BROWN GRE)																	
31010	C.I. DIRECT BROWN 1:2									- - - -	- - - -		CAP					
30115	DIRECT DYE (DIAMINE BROWN GNE)																	
31020	C.I. DIRECT BROWN 154	- - - -	- - - -		ACS,FAB	- - - -	- - - -		ACS, FAB	- - - -	- - - -		ACS,FAB	- - - -	- - - -		FAB	
30125	C.I. DIRECT BROWN 68																	
30245	C.I. DIRECT BLACK 4	- - - -	5		ACS,FAB,CAP	- - - -	- - - -		FAB,CAP	- - - -	- - - -		FAB,CAP	- - - -	- - - -		FAB,CAP	
31540	DIRECT DYE (PLUTO BLACK TG EXTRA)																	
31545	C.I. DIRECT BLACK 10																	
31565	C.I. DIRECT BLACK 9	23	17		AC,ACS,ATL,DUP	- - - -	- - - -		ACS,ATL,DUP									
31715	DIRECT DYE (CHROMANIL BROWN GG)																	
31875	DIRECT DYE (COLUMBIA BLACK B)																	
31880	DIRECT DYE (BENZO CHROME BLACK G)																	
31940	DIRECT DYE (COLUMBIA BLACK B)																	
35045	DIRECT DYE (TOLUYLENE BROWN B)																	
35260	C.I. DIRECT BLACK 28																	
35450	DIRECT DYE (PLUTO BLACK G)																	
35660	C.I. DIRECT BROWN 31	- - - -	14		ACS,ATL,CAP	33	33			21.3	19.1		ACS,ATL,FAB,CAP	- - - -	- - - -		FAB,CAP	
35670	DIRECT DYE (TRISULFON BROWN G)																	
35680	DIRECT DYE (TRISULFON BROWN 2G)																	
46020	C.I. BASIC YELLOW 7																	
46025	BASIC DYE (ACRIDINE YELLOW GAMD Y)																	
46040	C.I. BASIC YELLOW 9			0.2														
46065	BASIC DYE (BENZOFLAVINE)																	
46080	BASIC DYE			0.02				0.1								0.05		0.2
50040	C.I. BASIC RED 5																	
53050	C.I. SULPHUR ORANGE 1																	

FIGURES ARE FROM THE UNITED STATES INTERNATIONAL TRADE COMMISSION, 1974 THROUGH 1978

1 INCLUDES DYES WHICH ARE SIMILAR TO, BUT NOT CHEMICALLY IDENTICAL WITH, THE INDICATED COLOUR INDEX NAME.

— DATA REPORTED IN CONFIDENCE OR NOT REPORTED

TABLE 3.5 DYES PRODUCED FROM 2,4-DIAMINOTOLUENE (continued)

C.I. NUMBER	C.I. NAME	1974				1975				1976				1977				1978
		PRODUCTION (U.S.) [1] [2]	SALES (U.S.) [1] [2]	IMPORTS (U.S.) [2]	MANUFACTURERS (U.S.)	PRODUCTION (U.S.) [1] [2]	SALES (U.S.) [1] [2]	IMPORTS (U.S.) [2]	MANUFACTURERS (U.S.)	PRODUCTION (U.S.) [1] [2]	SALES (U.S.) [1] [2]	IMPORTS (U.S.) [2]	MANUFACTURERS (U.S.)	PRODUCTION (U.S.) [1] [2]	SALES (U.S.) [1] [2]	IMPORTS (U.S.) [2]	MANUFACTURERS (U.S.)	IMPORTS (U.S.) [2]
53051	C.I. SOLUBILISED SULPHUR ORANGE 1																	
53055	C.I. SULPHUR BROWN 10																	
53055	C.I. LEUCO SULPHUR BROWN 10	- - - -	- - - -		SDC	- - - -	- - - -		SDC	- - - -	- - - -		SDC	- - - -	- - - -	0.07	SDC	
53056	C.I. SOLUBILISED SULPHUR BROWN 10																	
53060	C.I. SULPHUR BROWN 2																	
53065	C.I. SULPHUR BROWN 21			0.3														
53065	C.I. LEUCO SULPHUR BROWN 21															0.1		
53066	C.I. SOLUBILISED SULPHUR BROWN 21																	
53070	C.I. SULPHUR BROWN 54																	
53075	C.I. SULPHUR BROWN 23																	
53075	C.I. LEUCO SULPHUR BROWN 23																	
53080	C.I. SULPHUR BROWN 22																	
53085	C.I. SULPHUR BROWN 39																	
53090	C.I. SULPHUR BROWN 26																	
53091	C.I. SOLUBILISED SULPHUR BROWN 26																	
53095	SULPHUR DYE (IMMEDIAL ORANGE PR)																	
53100	C.I. SULPHUR BROWN 30																	
53105	C.I. SULPHUR YELLOW 6																	
53105	C.I. SULPHUR ORANGE 3																	
53106	C.I. SOLUBILISED SULPHUR ORANGE 3																	
53115	C.I. SULPHUR BROWN 19																	
53130	SULPHUR DYE (IMMEDIAL YELLOW BROWN D)																	
53135	C.I. SULPHUR BROWN 55																	
53175	C.I. SULPHUR GREEN 8																	
53295	C.I. SULPHUR BLACK 6																	
53295	C.I. LEUCO SULPHUR BLACK 6																	
76035	C.I. OXIDATION BASE 20																	
76035	C.I. DEVELOPER 14																	
76036	OXIDATION BASE																	

FIGURES ARE FROM THE UNITED STATES INTERNATIONAL TRADE COMMISSION 1974 THROUGH 1978

[1] INCLUDES DYES WHICH ARE SIMILAR TO, BUT NOT CHEMICALLY IDENTICAL WITH, THE INDICATED COLOUR INDEX NAME

--- DATA REPORTED IN CONFIDENCE OR NOT REPORTED

53090	C.I. LEUCO SULFUR BROWN 26	STC	STC

AC AMERICAN COLOR AND CHEMICAL CORP

ACS ALLIED CHEMICAL CORP., SPECIALITY CHEMICAL DIVISION

ACY AMERICAN CYANAMID CO.

DSC DYE SPECIALTIES, INC.

DUP E.I. DUPONT DE NEMOURS & CO., INC.

FAB FABRICOLOR MANUFACTURING CORP.

GAF GAF CORP.

KCW KEYSTONE COLOR WORKS, INC.

KOH H. KOHNSTAMM & CO., INC.

PSC, PASSAIC COLOR AND CHEMICAL CO.

SDC MARTIN-MARIETTA CORP., SODYECO DIV.

STC AMERICAN HOECHST CORP., SOU-TEX WORKS

TRC TOMS RIVER CHEMICAL CORP.

TABLE 3.6 ESTIMATE OF THE MAXIMUM AMOUNT OF 2,4-DIAMINOTOLUENE DYES PRODUCED

Amount of 2,4-DAT Dyes By Dye Category	1974	1975	1976	1977
BASIC	312 kkg (0.25%)	2032 kkg (2.17%)	2139 kkg (1.84%)	3346 kkg (2.79%)
DIRECT	2582 (2.07%)	776 (0.83%)	790 (0.68%)	1739 (1.45%)
SOLVENT	1622 (1.30%)	1822 (1.95%)	2441 (2.10%)	180 (0.15%)
MORDANT	62 (0.05%)	56 (0.06%)	81 (0.07%)	276 (0.23%)
SULFUR*	9057 (7.26%)	7589 (8.12%)	9229 (7.94%)	10134 (8.47%)
SULFUR*	911 (0.73%)	757 (0.81%)	918 (0.79%)	1019 (0.85%)
TOTAL (100% SULFUR)	13635 (10.93%)	12275 (13.13%)	14680 (12.63%)	15675 (13.09%)
TOTAL (10% SULFUR)	5489 (4.4%)	5443 (5.82%)	6369 (5.48%)	6560 (5.47%)

Figures for calculations are from the United States International Trade Commission 1974 Through 1977.

*Sulfur dyes appeared under the category "all other dyes" which also included azoic compositions, azoic coupling components, and miscellaneous dyes. Two assumptions were made: either the sulfur dyes made up the entire category (100% figures) or they made up 10% of the category. As a result, there are two estimates for the sulfur dyes and the total amount of dyes made from 2,4-DAT.

Some of the producers of 2,4-DAT dyes are shown in the map in Figure 3.3. The majority of the producers are in the Eastern portion of the United States with New Jersey having the greatest number. Four of the seven major dye manufacturers are located in the New Jersey-Delaware area (Industrial Process Profiles for Environmental Use, 1977): Allied Chemical Corporation, American Cyanamid Company, E.I. du Pont de Nemours & Company, Inc., and Toms River Chemical Corporation.

In general, organic dyes are synthesized by the chemical conversion of one or more intermediates into a new compound (Shreve and Brink, 1977). These processes produce a variety of gaseous, liquid and solid wastes including excess reactants, intermediates, reaction by-products, organic vapors such as amines and phosgene, residues, filters and dyes (Industrial Process Profiles for Environmental Use, 1977).

The majority of the 2,4-DAT dyes are produced via diazotization. At the end of this process, the reaction solution is filtered, and the filtrate containing some 2,4-DAT eventually enters the waste stream. The filter is probably discarded in a landfill and will also contain some 2,4-DAT and dye.

Approximately 2,100 kkg of 2,4-DAT are consumed in the production of dyes (see Table 3.1, footnote 13). Some of this will remain in the dyes as a contaminant and 172 kkg will be released to air (2 kkg), land (20 kkg to landfill), and water (150 kkg). (See Table 3.1).

3.5 RELEASES FROM DYE PROCESSES

Dyes produced from 2,4-DAT are used to color textiles (cotton, wood, silk and synthetic fabrics) and leather. It is estimated that 840 kkg of 2,4-DAT are used to produce dyes for the textile and leather industries (40% of the total amount of 2,4-DAT used to manufacture dyes) (see Table 3.1, footnote 15). Five percent (40 kkg) is estimated to remain as a contaminant in the dyes. The dyeing operations are performed in large baths with the liquid being discharged to municipal sewer systems after the dyeing is completed. It is estimated that 90% (36 kkg) of the 2,4-DAT present as a contaminant is lost in the waste stream while the remaining 10% (4 kkg) is landfilled from filtering residues.

FIGURE 3.3 PRODUCERS OF 2,4-DIAMINOTOLUENE DYES
(United States International Trade Commission, 1974-1977)

Allied Chemical Corporation Chemical Division	Morristown, NJ
American Color and Chemical Corporation	Reading, PA
American Cyanamid Company	Wayne, NJ
E.I. du Pont de Nemours & Co., Inc.	Wilmington, DE
Dye Specialties, Inc.	Jersey City, NJ
Fabricolor Manufacturing Corporation	Paterson, NJ
GAF Corporation	Chattanooga, TN Rensselar, NY
Keystone Color Works, Inc.	York, PA
H. Kohnstamm & Company, Inc.	New York, NY
Passaic Color and Chemical Company	Paterson, NJ
Martin-Marietta Corporation, Sodyeco Div.	Charlotte, NC
Toms River Chemical Corporation	Toms River, NJ

2,4-DAT has also been used as a developer for permanent oxidative hair dyes. These hair dyes function as follows: the aromatic amines are oxidized to imines which react with color modifiers to form dyes. It is estimated that 5 kkg of 2,4-DAT was consumed for hair dyeing operations. During the dyeing process, up to one percent of the chemicals are absorbed (Ames et al., 1975); this means 0.05 kkg 2,4-DAT is absorbed in one year. The remaining 99% either reacts to form the dye or remains unreacted and is discharged to the sewer system. Assuming the reaction is 95% complete, 4 percent (0.2 kkg) will be discharged to the sewer. (See Table 3.1, footnote 20).

Wood stains, biological stains, and indicators also contain dyes made from 2,4-DAT (World Health Organization, 1978). These dyes are also used to color plastic, industrial antiseptic, and industrial paints (Industrial Process Profiles for Environmental Use, 1977). These miscellaneous uses constitute almost 60% of the 2,4-DAT dye usage (leather, hair, and textile dyes are estimated to use 40% of the 2,4-DAT dyes). 2,4-DAT would be a contaminant of these dyes, presumably in the same quantity (5%) as is estimated to be present in the dyes for leather and textiles. The majority of the 2,4-DAT in the waste from the use of these dyes would be discharged to the municipal sewer system (See Table 3.1, footnote 21).

2,4-DAT is used as a developer for some dyes in order to obtain dark shades. It is used directly in the dye bath and the amount present varies according to the color desired. As a result, 2,4-DAT will be present in the waste stream of such dyeing operations in an unknown amount. Because of the low vapor pressure of 2,4-DAT, it is believed that little 2,4-DAT is released to the atmosphere (Comer et al., 1979).

3.6 RELEASES DURING EXPORT OF 2,4-DIAMINOTOLUENE

Information on the quantities of 2,4-DAT exports was not obtained. The quantities of this compound exported appear to be unknown (Gunn and Cooke, 1976).

4.0 RELEASES FROM INDIRECT SOURCES OF DIAMINOTOLUENE

2,4-Diaminotoluene is produced indirectly by four routes. Toluene diisocyanate and polyurethane foams can both be hydrolyzed to 2,4-DAT. In addition, 2,4-DAT may be produced through the metabolism of 2,4 DNT. 2,4-DAT may also be obtained during the degradation of the dyes produced from it.

4.1 HYDROLYSIS OF TOLUENE DIISOCYANATE

A common reaction of toluene diisocyanate is its reaction with water to form diaminotoluene. Since CO_2 is released in this reaction, it can be used in the production of foam products. The diaminotoluene produced can be further reacted with toluene diisocyanate to form a polymer (Lowe, 1970; Kirk-Othmer, 1969; Simonds and Church, 1967). The reaction of TDI and water occurs rapidly and precautions must be taken against any contact of TDI with humidity in the air (Simonds and Church, 1967).

For these reasons, we have assumed that any TDI which is released to the environment would be rapidly hydrolyzed to DAT. In addition, scrubbers are used to trap TDI which is emitted from polyurethane resin manufacture and convert it to DAT (Smith and LaShelle, 1974).

We have estimated (Table 4.1) that 2800 kkg of 2,4-DAT may be produced from this process annually. This calculation was based on releases of TDI from TDI production, TDI export and TDI foam use. Since other releases may occur, this number is expected to be a minimum. Losses occur to air, land and water (Table 4.1).

4.2 HYDROLYSIS OF POLYURETHANE FOAMS

In addition to hydrolysis of TDI, hydrolysis of foams produced from TDI occurs in warm, humid environments (Guthrie and McKinney, 1977; Phillips and Parker). The rate of degradation of foams is dependent upon the type of polyurethane and the conditions to which the foam is exposed. For these reasons, it is difficult to estimate the rate of production of 2,4-DAT due to polyurethane foam hydrolysis. Although some hydrolysis of newly produced foams would have occurred during the first year after production, significant amounts of foam

TABLE 4.1 RELEASES FROM INDIRECT SOURCES

PROCESS	AMOUNT OF 2,4-DAT PRODUCED (kkg)	POINT SOURCES OF RELEASES	QUANTITIES STORED (kkg)	RELEASES TO THE ENVIRONMENT					
				AIR		LAND		WATER	
				Amt (kkg)	Form	Amt (kkg)	Form	Amt (kkg)	Form
Hydrolysis of TDI	≥ 2800[5]	• Residue from TDI manufacture	60[1] in landfill	3[1]	Free				
		• Ventilation system losses during TDI manufacture		190[2]	Free			2000[2]	Free
		• Release of TDI during use of polyurethane foams		50[3]	Free				
		• Losses during export		340[4]	Free			170[4]	Free
Hydrolysis of Polyurethane Foams	Unknown	• Foam produced during the year							
	Unknown	• Stockpiled foam							
	Unknown	• In use							
	Unknown	• In Landfill							
Metabolism of 2,4-DNT	Unknown	• Animals and Microorganisms				Free or sulfate and glucuronide conjugates		Free or sulfate and glucuronide conjugates	
Degradation of Dyes	Unknown	• Dyed products					Free		Free
	Unknown	• Waste streams from dye manufacturing					Free		Free

Table 4.1 Footnote

1. In Table 3.1 (footnote 4) 133 kkg of isocyanates were calculated to be released in the residue from TDI manufacture. Of this amount, 50% might be incinerated (Table 3.1, footnote 5). Of this 50% (67 kkg), about 5% could be released to air during incineration resulting in a net loss to air of 3 kkg. Another 50% of the residue (67 kkg) would be landfilled. Of this, probably 95% would be hydrolyzed to 2,4-DAT (3 kkg to air, 60 kkg to landfill).

2. Losses through the ventilation system during TDI manufacture were estimated from the 229,000 kkg of TDI produced. We estimate that 1% of the TDI produced may be released to air since TDI is moderately volatile and is present in high concentrations. This amount is 2,300 kkg. Since TDI has a low solubility in water, we estimate that only about 90% of the amount would be lost to water through the scrubber system. Therefore, 200 kkg of TDI would be released to air and 2,100 to water. If hydrolysis occurred to 95%, amounts of 2,4-DAT produced would be 190 kkg in air and 2,000 kkg in water.

3. Amounts of TDI released from polyurethane foams is estimated at 50 kkg based on the fact that approximately 200 times more TDI than DAT should be present in these foams. Although 1 kkg of DAT was estimated to be released from foams (Table 3.1, footnote 2) some fraction of this release is probably due to hydrolysis of the foams. The 50 kkg of TDI released would be lost to air. If 95% of the TDI is hydrolyzed to 2,4-DAT, this amount would be 50 kkg of 2,4-DAT.

4. Export losses may be expected to be up to 2% of the TDI exported. Since approximately 27,000 kkg of TDI are exported (Table 3.1, footnote 6), this amount lost during export would be 540 kkg. If 95% of this is hydrolyzed to 2,4-DAT, 510 kkg of 2,4-DAT would result from this process. Of this 510 kkg, it is estimated that 340 kkg would be lost to air and 170 kkg would be lost to water.

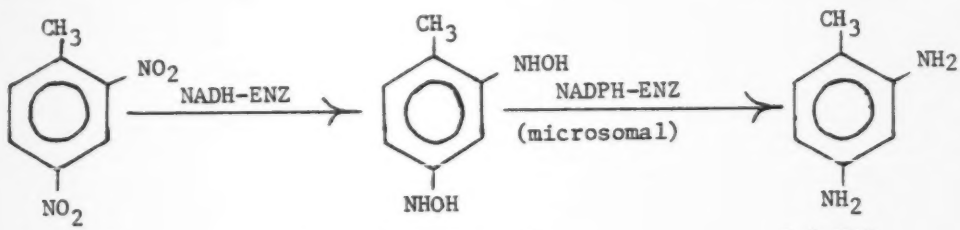
5. The total of 2,4-DAT production by hydrolysis of TDI is estimated to be greater than 2,800 kkg. This amount is the total of 2,4-DAT produced by the various sources discussed in footnotes 1-4.

hydrolysis probably occur in foam which has been stockpiled from previous years. Foam hydrolysis may occur during use or after disposal in landfills.

Sufficient information on the hydrolysis of polyurethane foams was not obtained to make an estimate of amounts of 2,4-DAT which may be produced by this process. However, we would estimate that this would be a significant source of release of 2,4-DAT to the environment.

4.3 METABOLISM OF 2,4-DINITROTOLUENE

The general mechanism of production of 2,4-DAT from 2,4-dinitrotoluene (2,4-DNT) in the mammalian liver is known as the nitroreductase system. An equation for this process is shown below (Fouts and Brodie, 1957; Kato et al., 1969):



2,4-DNT — 2,4-dihydroxyamino-toluene — 2,4-DAT

Between 5 and 13% of the 2,4-DNT metabolized by mammals is converted to 2,4-DAT (Mammalian Toxicity of Munitions Compounds, 1978). Most of these metabolites appear as glucuronide conjugates with smaller amounts of sulfate conjugates or free 2,4-DAT being produced.

2,4-Dinitrotoluene is produced in significant quantities (94,000 kkg in 1977; U.S. International Trade Commission, 1978) for use in the production of 2,4-DAT and TNT. Any amounts of DNT which would be absorbed, inhaled or ingested by mammals could undergo metabolism and 2,4-DAT could be produced as a metabolite.

In addition to metabolism by mammals, microorganisms may be a significant source of 2,4-DAT production through metabolism of 2,4-DNT. Anaerobic bacteria appear to be able to metabolize 2,4-DNT to 2,4-DAT. In addition, a similar mechanism for metabolism in Mucosporium sp., a fungus, was proposed (McCormick et al., 1968). If microorganisms are indeed capable of producing 2,4-DAT from from 2,4-DNT, the amount of 2,4-DAT produced may be significant.

4.4 DEGRADATION OF DYES

To determine if the degradation of dyes is a significant source of 2,4-DAT, the structure of the various dyes produced from 2,4-DAT was examined (Colour Index, 1971). Of the 67 dyes produced from 2,4-DAT, approximately 30 dyes might be expected to be degraded into 2,4-DAT. These include Basic Brown 4 (C.I. # 21010), Solvent Brown 12 (C.I. # 21010:1), Diphenyl Fast Black (C.I. # 25070) and the various sulfur dyes.

Of the 2,4-DAT dyes which may be degraded to produce 2,4-DAT, the sulfur dyes and Diphenyl Fast Black are probably not of great significance since they appear to be produced and imported in small quantities. In addition the exact structure of the sulfur dyes is unknown, so it is difficult to determine their potential for degradation to 2,4-DAT. The other two dyes, Basic Brown 4 and Solvent Brown 12, have been produced in moderate quantities in the past (227 kkg in 1974; U.S. International Trade Commission, 1976). However, since at the maximum only 33% of this dye would be expected to be degraded to 2,4-DAT, this source of 2,4-DAT appears to also be of little significance.

5.0 RELEASE SOURCE EVALUATION

The total releases from the production and use of 2,4-DAT to the environment in 1977 are estimated to be at least 10,618 kkg (by summation of the releases in Figure 1). The production of 2,4-DAT, hydrolysis of TDI, production of dyes, and the use of dyes contaminated with 2,4-DAT accounted for 99.7% of the releases to the environment. The remaining 0.3% of the releases came from TDI production, exports of TDI, imports of 2,4-DAT and the use of polyurethanes.

The majority of the releases (6225 kkg or 59 %) went to land with releases to water accounting for 35 % (3654 kkg) and releases to air, 7% (739 kkg). Hydrolysis of TDI and the production of 2,4-DAT accounted for 99% (732 kkg) of the releases to air. However, 2,4-DAT production is estimated to produce 98 % (6127 kkg) of all the releases to land. Hydrolysis of TDI, 2,4-DAT production, and dye production account for 97% (3546 kkg) of the releases to water. (See Table 5.1 for a breakdown of the release sources and their contribution to the total releases.)

From the information in Table 5.1 it appears that the production of 2,4-DAT and the hydrolysis of TDI are the two major sources of releases to the environment. Since the majority (82%) of 2,4-DAT produced from the hydrolysis of TDI occurs at the TDI plant (this was estimated from the release information in Table 4.1), any area where there is a concentration of TDI manufacturing plants or TDI and 2,4-DAT manufacturing plants is a potentially important source for large quantities of 2,4-DAT to be released to the environment. A concentration of 2,4-DAT plants is also a potentially important source of large 2,4-DAT losses to the environment.

There are several areas where 2,4-DAT and TDI manufacturing plants are concentrated (see Figure 2.2 and Figure 3.1). The largest concentration is in West Virginia. Rubicon and Union Carbide each have a 2,4-DAT manufacturing plant in Institute, West Virginia and South Charleston, West Virginia. Union Carbide also produces TDI in both cities. Mobay and Allied Chemical each have a plant in West Virginia and these plants produce 2,4-DAT and TDI.

TABLE 5.1 BREAKDOWN OF RELEASE SOURCES

Total Releases

1. production of 2,4-DAT	7502 kkg	97%	
2. hydrolysis of TDI	2813		
3. dyes production	172		99.7%
4. dye usage (contamination)	100		
5. TDI production	25		
6. exports of TDI	3		
7. imports of 2,4-DAT	2		0.3%
8. use of polyurethane foams	1		
	10618 kkg		

Releases to Air

1. hydrolysis of TDI	583 kkg	99%	
2. 2,4-DAT production	149		
3. dye production	2		
TDI production	1		1%
TDI exports	2		
4. imports of 2,4-DAT	1		
use of polyurethane foams	1		
	739 kkg		

Releases to Land

1. 2,4-DAT production	6127 kkg	98%	
2. hydrolysis of TDI	60		
3. dye production	20		
4. due usage	10		2%
5. TDI production	7		
6. exports of TDI	1		
	6225 kkg		

TABLE 5.1 BREAKDOWN OF RELEASE SOURCES (continued)

Releases to Water

1.	hydrolysis of TDI	2170 kkg	97%
2.	2,4-DAT production	1226	
3.	dye production	150	
4.	dye usage	90	3%
5.	TDI production	17	
6.	imports of 2,4-DAT	1	
		3654 kkg	

Louisiana is another potentially important area of release. Olin Corporation has a 2,4-DAT manufacturing plant in Geismar, Louisiana. Rubicon also has a TDI manufacturing plant in Geismar as does BASF Wyandotte. A 2,4-DAT and TDI manufacturing plant is operated by Olin Corporation in Lake Charles, Louisiana.

6.0 DATA GAPS AND RECOMMENDATIONS

In preparing a materials balance for 2,4-DAT, many data gaps were encountered. This was due either to the lack of research, lack of monitoring data, the fact that much of the industrial information examined was classified as confidential, and incomplete literature on pertinent subjects. The difficulties and lack of information in specific areas of the materials balance are delineated in the following sections. Where appropriate, recommendations as to methods of remedying these gaps in data are made.

6.1 MANUFACTURE OF 2,4-DIAMINOTOLUENE

The major problem encountered in attempting to obtain the yearly production figures for 2,4-DAT was the fact that most 2,4-DAT produced is captively consumed. This problem was circumvented by calculating the amount of 2,4-DAT used in the products made from 2,4-DAT. However, accurate production data is needed to establish a precise materials balance for 2,4-DAT. In addition to knowing the total quantity of 2,4-DAT produced, it is also necessary to estimate the amount produced by each of the different industrial processes and the quantities of the different isomeric (2,4 and 2,6) mixtures (80/20, 65/35, and 100) produced. This information may be acquired by contacting the producers of 2,4-DAT.

The purity and types of impurities contained in 2,4-DAT consumed by the production of toluene diisocyanate and dyes was not available in the literature. This information is important in order to determine the amount of 2,4 DAT that is actually a contaminant of an end product. The information may best be acquired by contacting the quality control office of 2,4-DAT manufacturers.

The literature reviewed revealed only one 2,4-DAT production flow diagram (Howard et al., 1976). However, no explanation was found as to the manner in which the processes or machinery functioned. In order to calculate the amount of 2,4-DAT lost during production, it is necessary to have an understanding of how the processes and equipment in the manufacturing process operate. This information could probably be obtained by searching the

literature, supplemented by contacts with industry.

The literature did not contain any references or data as to the quantity, composition and dispositon of 2,4-DAT generated during production. This information is crucial to obtaining an accurate estimate of 2,4-DAT releases to the environment. The most accurate data could be obtained by monitoring factory releases.

We could not determine the fate of 2,4-DAT subsequent to its manufacture and prior to its use in the processing of TDI and dyes. Information on its transport and/or storage was lacking. Industry contact would best yield data in these areas.

6.2 IMPORTS OF 2,4-DIAMINOTOLUENE

Although data on the amounts of 2,4-DAT imported into the U.S. were located, no information on which companies were responsible for this importation was found. This information, if it is not proprietary, might be derived from personal contact with the U.S. International Trade Commission. Similarly, knowledge of which cities receive imports of 2,4-DAT would be useful in evaluating releases of the compound on a geographic basis.

Certainly data on the types and amounts of losses due to imports would be integral to an accurate materials balance on 2,4-DAT. This kind of information could be obtained by first identifying importing companies and ports, and then sampling for releases of 2,4-DAT.

6.3 EXPORTS OF 2,4-DIAMINOTOLUENE

Several data gaps in the area of export of 2,4-DAT are apparent. Most importantly, information as to the quantities of 2,4-DAT exported are unavailable and would be highly useful. Without this data, it is extremely difficult to estimate any amounts of releases. If the amounts exported could be identified, possibly by personal contact with the U.S. International Trade Commission, and the geographic locations of export as well, then monitoring could be implemented to determine types and amounts of releases of 2,4-DAT.

6.4 2,4-TOLUENE DIISOCYANATE PRODUCTION

The most serious lack of information on the production of 2,4-TDI is in the area of the manufacturing process. Data on points and amounts of 2,4-DAT released during production could be obtained by site visits and monitoring, releases during

the manufacturing process and the subsequent operations such as incineration and wastewater disposal could be identified.

In addition, information on the storage of 2,4-TDI would be useful. From this knowledge, amounts of 2,4-DAT due to storage could be better estimated. Monitoring would provide more accurate data. Similarly, information on quantities of 2,4-TDI transported and possible resultant release of 2,4-DAT would be helpful in establishing a better materials balance.

6.5 IMPORTS OF 2,4-TOLUENE DIISOCYANATE

We were unable to locate any information on importation of 2,4-TDI. Valuable data would include quantities imported, companies responsible for importation, the geographic areas involved, and finally, the types and amounts of releases of 2,4-TDI. From this, it might be possible to estimate what portion of releases is composed of 2,4-DAT. The kind of information needed might be gathered in the same way as the import/export data for 2,4-DAT.

6.6 EXPORTS OF 2,4-TOLUENE DIISOCYANATE

The same type of information required to calculate 2,4-DAT releases due to import of 2,4-TDI is needed to estimate 2,4-DAT exposure due to export of 2,4-TDI. Again, little data could be obtained on this subject.

6.7 MANUFACTURE OF PRODUCTS FROM 2,4-TOLUENE DIISOCYANATE

Monitoring data on the releases of 2,4-DAT during the manufacture of polyurethane foams and other polyurethane products would be necessary in order to establish an accurate 2,4-DAT materials balance.

We were unable to locate any information relative to the 2,4-TDI, and consequently, 2,4-DAT content, of any nonpolyurethane product of which 2,4-DAT is a component. Therefore, there was no effective way of estimating the 2,4-DAT releases from such products.

Industry contacts and an in-depth study of the manufacturing processes involved - as well as sampling for releases, are indicated to fill in the data gaps in these areas.

6.8 USES OF POLYURETHANE PRODUCTS

Aside from the Guthrie and McKinney (1977) report on the 2,4-DAT content of commercial polyurethane foams, we encountered no information as to the potential release of the compound from foams. We assume that a certain amount of foam is landfilled each year, that a certain quantity of foam is already stored in landfill, and that the 2,4-DAT found in these foams is released at a particular rate. However, there is no data concerning any of these areas. An examination of the amount of polyurethane foam in landfills, and further research into the rate of release of 2,4-DAT in foams is indicated here.

In addition, the process of amine recovery from foam should be scrutinized. This could be accomplished by literature searches, patent searches and industry contacts in order to determine if the process is being used, and if so, the quantities of 2,4-DAT being recovered.

Little information relative to release of 2,4-DAT from the use of other polyurethane products was located. As previously mentioned, we were unable to find out exactly how much 2,4-DAT was a contaminant in these products.

6.9 DYE PRODUCTION

Information on the amount of 2,4-DAT used in the production of dyes as well as information on the actual manufacturing processes involved is needed to determine the releases of 2,4-DAT from this industry. Sources of this information might be personal contacts with industry, site visits, and monitoring of the industrial wastestream. However, much of this information is proprietary and the specific dye formulations are often considered trade secrets. Data on the losses due to the shipping of 2,4-DAT to dye manufacturing facilities as well as the handling and storage of 2,4-DAT might be obtained from manufacturers of 2,4-DAT, dye manufacturers, or trade associations.

6.10 IMPORTS OF DYES

Little information was available on the importation of dyes produced from 2,4-DAT. Information on the entry ports as well as the manner of shipping and storage would be useful in the evaluation of the releases of dyes containing

2,4-DAT as a contaminant. Import agents and the U.S. International Trade Commission are possible sources of this data. Contacts with industry may also provide this information as well as identifying which companies in the United States use these dyes and in what quantities.

6.11 EXPORTS OF DYES

The following information needs to be determined to evaluate 2,4-DAT losses from the exports of dyes contaminated with 2,4-DAT: companies which export the dyes; methods of shipping, handling, and storage; and losses during shipping, handling, and storage. Knowledge of ports used for exporting would also be useful for a geographical evaluation of 2,4-DAT releases. This information could be obtained in the same manner as the information for imports.

6.12 DYE USAGE

Information on the amount of 2,4-DAT present as a contaminant in dyes is important for the determination of its loss from dyeing operations. This could be determined through the evaluation of the dye production process or through contacts with industry. Also needed to be determined are the actual amounts of 2,4 DAT dyes used for dyeing processes and which industries use them. This information might be obtained from industry or trade associations however, much of this information may be considered proprietary. Monitoring data for the dye industry would also be important in the evaluation of 2,4-DAT release.

Since the amount of 2,4-DAT used as a dye developer in the dyeing process is not known, more information in this area is needed. Industry contacts may supply data on the quantities of 2,4-DAT used, the reaction process, how much remains unreacted, and the losses of 2,4-DAT from the process.

Further studies need to be performed on the current use of 2,4-DAT in oxidative hair dyes. The following information should be determined: whether 2,4-DAT is currently used in hair dyes, how much is used, the yield of the reaction, how many people dye their hair, and how often the hair is dyed. Contacts with hair dye manufacturers and trade associations may provide pertinent data.

6.13 INDIRECT SOURCES OF 2,4-DIAMINOTOLUENE

In order to accurately estimate the amounts of 2,4-TDI which can potentially be hydrolyzed to 2,4-DAT, it would most likely be necessary to perform a materials balance on 2,4-TDI and identify all of the points and amounts of release of that compound. It would be necessary to find out how much 2,4-TDI is hydrolyzed to 2,4-DAT, and how much of this is lost to the environment, and where.

The hydrolysis of polyurethane foams is a potentially significant source of 2,4-DAT, but as previously mentioned, there is little data on this subject. Similarly, the metabolism of 2,4-DNT to 2,4-DAT is another important source of the compound, but with little available information. It would be useful to determine if microorganisms metabolize 2,4-DNT to 2,4-DAT and under what conditions, since this metabolism might be a significant source of 2,4-DAT. To further complicate the situation, extensive information on releases of 2,4-DNT would be required to accurately estimate amounts of 2,4-DAT formed from the metabolism of 2,4-DNT. Dye degradation might be another source of indirect production of 2,4-DAT, but as explained in the section on data gaps pertaining to dyes, we were unable to identify which 2,4-DAT dyes are manufactured, the amounts made and the quantities produced over the years. We also do not know how much of the dyes degrade to 2,4-DAT, and at what rate.

LITERATURE CITED

Ames, B. N., Kammen, H.O. and Yamasaki, E., "Hair Dyes are Mutagenic: Identification of a Variety of Mutagenic Ingredients," Proceedings of the National Academy of Sciences, June 1975, pp. 2423 - 2427.

Austin, G.T. "Industrially Significant Organic Chemicals Part 9," Chemical Engineering, Vol. II, 1974, pp. 96-100.

Automatic Exchange Resin Pilot Plant for Removal of Textile Dye Wastes, EPA-600/2-77-136, July 1977.

Campbell, G.A. and Meluch, W. C., "Polyurethane Waste Disposal Process Development: Amine Recovery," Journal of Applied Polymer Science, Vol. 21, 1977, pp. 581-584.

Cardy, R.H., "Carcinogenicity and Chronic Toxicity of 2,4 - Toluene-diamine in F-344 Rats, " Journal of the National Cancer Institute, Vol. 62, #4, 1979, pp. 1107 - 1116.

Chemical Market Abstracts, Vol. 69, No. 3, March 1977, p.182.

Chemical Market Abstracts, Vol. 69, No. 4, April 1977, pp. 91-92,142.

Chemical Market Abstracts, Vol. 69, No. 5, May 1977, p. 100.

Chemical Market Abstracts, Vol. 69, No. 6, June 1977, p. 118.

Chemical Market Abstracts, Vol. 69, No. 8, August 1977, pp. 91, 191.

CIIT Current Status Reports, No. 2, Dinitrotoluene (Technical), Chemical Industry Institute of Toxicology, May 1977.

Colour Index, The Society of Dyers and Colourists, 3rd ed., Vol. 4, 1971.

Comer, R., Chen, A., and Lee, A. Toluene 2,4-diamine CAS Registry No. 95-80-7, JRB Associates, Inc. 1979.

Considine, Douglas M., ed. Chemical and Process Technology Encyclopedia, McGraw-Hill Book Co., 1974.

Directory of Chemical Producers, Stanford Research Institute, 1977.

Dombrow, B. Z. Polyurethanes, 2nd ed., Reinhold Publishing Corporation, 1965.

Environmental Protection Agency Chemical Hazard Information Profile, Toluene - 2,4 - diamine, Chemical Information Division.

Fouts, J. R., and Brodie, B. B. "The enzymatic reduction of chloramphenicol, P-nitrobenzoic acid and other aromatic nitro compounds in mammals," Journal of Pharmacology and Experimental Therapeutics, Vol. 119, 1957, pp. 197-206.

Gunn, T. C., and Cooke, S. E. "Toluene," Chemical Economics Handbook, Stanford Research Institute, Menlo Park, Calif. 1976.

Guthrie, J. L. and McKinney, R. W. "Determination of 2,4 - and 2,6 - Diaminotoluene in Flexible Urethane Foams," Analytical Chemistry, Vol. 49, 1977, pp. 1676-1680.

Horning, Roderick H., ADMI/EPA Study of Dye Wastes. Presented at Textile Technology/Ecology Interface 1975. Sponsored by the American Association of Textile Chemists and Colorists.

Howard, P. H., Santodonata, J., Saxena, J., Malling, J., and Greninger, D., Investigation of Selected Potential Environmental Contaminants - Nitroaromatics, Syracuse Research Corp., N.Y. Center for Chem. Hazard Assessment. EPA-560/2-76-010. June 1964.

Industrial Process Profiles for Environmental Use: Chapter 7. Organic Dyes and Pigments Industry, EPA-600/2-77-023g, February 1977.

Jones, H. R., Pollution Control in the Textile Industry, Noyes Data Corp., 1973.

Kato, R., Oshima, T., and Takanaka, A. "Studies on the mechanism of nitro reduction by rat liver", Molecular Pharmacology, Vol. 5, 1969, pp. 487-498.

Kirk - Othmer Encyclopedia of Chemical Technology, 2nd revised ed., Vol. 13, 1964.

Kirk-Othmer Encyclopedia of Chemical Technology, 2nd revised ed., Vol. 13, 1969.

Lowe, A., "The Chemistry of Isocyanates" Proceedings of the Royal Society of Medicine Section of Occupational Medicine. Symposium on Isocyanates, Vol. 63, April 1970. p. 365.

Lowenheim, Frederick and Marguerite K. Moran, Faith, Keyes, and Clark's Industrial Chemicals, 4th ed., John Wiley and Sons Inc., 1975.

McCormick, N. G., Cornell, J. H., and Kaplan, A. M. "Identification of biotransformation products from 2,4 - dinitrotoluene," Applied and Environmental Microbiology, Vol. 35, 1978, pp. 945-949.

Mammalian Toxicity of Munitions Compounds Phase II: Effects of Multiple Doses Part II: 2,4-Dinitrotoluene, Midwest Research Institute, 1978.

Phillips, L. N. and Parker, D.B.V., Polyurethanes Chemistry, Technology and Properties, Iliffe Books Ltd.

Processes Research, Inc., Alternatives for Hazardous Waste Management in the Organic Chemical Pesticides and Explosives Industry, Cincinnati, Sept 1977.

Radding, S. B. et al. Assessment of Potential Toxic Releases from Leather Industry Dyeing Operations, EPA-600/2-78-215, October 1978.

Sax, N. I. Dangerous Properties of Industrial Materials, 4th ed., Van Nostrand Reinhold Co. 1975.

Shreve, R. N. and Brink, J. A., Jr. Chemical Process Industries, 4th ed., McGraw-Hill Book Co., 1977.

Simonds, H. R. and Church, J. M. (eds). The Encyclopedia of Basic Materials for Plastics. Reinhold Publishing Corp., 1967, pp. 141-145.

Sittig, M. Amines, Nitriles & Isocyanates Processes and Products. Noyes Development Corporation, 1969.

Smith, W. E. & LaShelle, S. R. Characterization of Atmospheric Emissions from Polyurethane Resin Manufacture, Midwest Research Institute, EPA 650/2-74-107, October 1974.

Stecker, P. G. (ed.), The Merck Index, 8th ed., Merck & Co. Inc., 1968.

Threlkeld, D. D. & Manno, P. S., "A changing U.S. isocyanate picture". Review & Forecast, Chemical Marketing Research Association, May 1977.

United States International Trade Commission, Imports of Benzenoid Chemicals and Products 1974, USITC Publication 762, 1976.

United States International Trade Commission, Imports of Benzenoid Chemicals and Products 1975, USITC Publication

United States International Trade Commission, Imports of Benzenoid Chemicals and Products 1976, USITC Publication 828, 1977.

United States International Trade Commission, Imports of Benzenoid Chemicals and Products 1977, USITC Publication 900, 1978.

United States International Trade Commission, Imports of Benzenoid Chemicals and Products 1978, USITC Publication 990, 1979.

United States International Trade Commission, Synthetic Organic Chemicals United States Production and Sales 1974, USITC Publication 776, 1976.

United States International Trade Commission, Synthetic Organic Chemicals United States Production and Sales 1975, USITC Publication 804, 1977.

United States International Trade Commission, Synthetic Organic Chemicals United States Production and Sales 1976, USITC Publication 833, 1977.

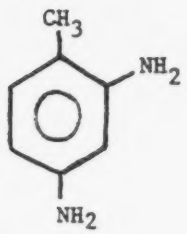
United States International Trade Commission, Synthetic Organic Chemicals United States Production and Sales 1977, USITC Publication 920, 1978.

Weast, R. C. (ed.), CRC Handbook of Chemistry and Physics, 58th ed., CRC Press, Inc., 1977.

World Health Organization. International Agency for Research on Cancer (IARC) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man: Some aromatic amines & related nitro compounds - hair dyes, colouring agents & miscellaneous industrial compounds. Vol. 16, January 1978.

APPENDIX A

Physical Characteristics of 2,4-Diaminotoluene (Weast, 1977)



$C_7H_{10}N_2$

Molecular weight: 122.17

Melting point: 99°C

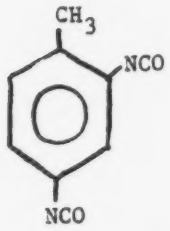
Boiling point: 280°C

Vapor pressure: 1 mm Hg at 106.5°C

Solubility in water:
alcohol: } very soluble
ether:

APPENDIX B

Physical Characteristics of Toluene Diisocyanate (Stecker, 1968)



Molecular weight: 174.5

Physical state: liquid at room temperature

Melting point: 19.5 - 21.5°C

Density (20°/4°C): 1.2244

Boiling point: 126°C

Flash point: 132°C (270°F)

Solubility in alcohol: miscible

Solubility in ether: miscible

Vapor Pressure: 0.01mm Hg at 20° C (Simonds and Church, 1967)